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DEVELOPMENT AND EVALUATION OF PROCEDURES FOR THE ANALYSIS OF SIMPLE CYANIDES, TOTAL CYANIDE, AND THIOCYANATE IN WATER AND WASTEWATER

by

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Seven methods for the analysis of simple cyanides have been investigated. Included are (1) an ion-exchange procedure, (2) a continuous-flow distillation, (3) and EDTA electrode method, (4) the American Iron and Steel Institute aeration method, (5) an EDTA aeration method, (6) the modified Roberts-Jackson method, and (7) the EPA procedure for Cyanides Amenable to Chlorination.

Of all of the procedures studied, the modified Roberts-Jackson method is the best. It gives complete recovery from all but one of the simple cyanides without decomposing the complex cyanides.

In addition to these methods for simple cyanides the EPA procedure has been evaluated for the analysis of total cyanide. Procedures using ligand-exchange and high temperature distillation have been developed and evaluated for analysis of total cyanides.

Colorimetric high performance liquid chromatography and atomic absorption spectrophotometric methods for the analysis of thiocyanates were investigated. All these methods are based on the formation and extraction of a thiocyanate-pyridine-copper (II) complex.

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ABSTRACT

This research program was initiated to develop and/or evaluate analytic test procedures for the analysis of simple cyanides, total cyanides, and thiocyanates.

Seven methods for the analysis of simple cyanides have been investigated. Included are (1) an ion-exchange procedure, (2) a continuous-flow distillation, (3) an EDTA electrode method, (4) the AISI aeration method, (5) an EDTA aeration method, (6) the modified Roberts-Jackson method, and (7) the EPA procedure for Cyanides Amenable to Chlorination. The methods that show the most promise are the EDTA aeration procedure, the modified Roberts-Jackson method, and the procedure for Cyanides Amenable to Chlorination.

Of all of the procedures studied, the modified Roberts-Jackson method is the best. It gives complete recovery from all but one of the simple cyanides without decomposing the complex cyanides. However, the most significant operating characteristic is its unique ability to perform accurately in the presence of both sulfide and thiocyanate.

In addition to these methods for simple cyanides, we have evaluated the U.S. EPA Method with an ion-selective electrode finish for the analysis of total cyanide, and have also developed and evaluated ligand-exchange and high temperature distillation procedures for the analysis of total cyanides. The ligand-exchange procedure appears to be the most advantageous method of analysis for total cyanides. It not only gives recoveries comparable to those found for the EPA method, but also is unaffected by the presence of either sulfide or thiocyanates. Analysis time is also reduced.

Methods investigated for the analysis of thiocyanates included colorimetric, high performance liquid chromatographic, and atomic absorption spectrophotometric methods. All these methods are based on the formation and extraction of a dithiocyanatodipyridylcopper(II) complex. None of the methods studied can accurately quantitate thiocyanate below 30 ppb.

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SECTION 1

INTRODUCTION

The Federal Water Pollution Control Act as amended after 1972, Section 304(h), requires that the administrator promulgate guidelines establishing test procedures for the analysis of pollutants. These test procedures must be applicable to measure a specific pollutant in a wide variety of industrial effluents. The objectives of this work were to review the pertinent literature to determine the technical approaches to be taken for development and evaluation of test procedures for analysis of cyanides and thiocyanates. Two new methods for total cyanide were developed and evaluated during this study and are compared with the EPA procedure for total cyanide. Three methods for thiocyanate were tested. These procedures depend on the chloroform extraction of the neutral dithiocyanatodipyridylcopper(II) complex to separate the SCN^- from the sample matrix. The thiocyanate was quantitated by colorimetry, high performance liquid chromatography, or graphite furnace atomic absorption spectroscopy. Statistical evaluation of the test results was obtained at several concentration levels for each of the methods studied. A description of the statistical protocol used in this study is given in Appendix F.

Six existing procedures for the analysis of simple cyanides were evaluated and compared to the Environmental Protection Agency (EPA) method "Cyanides Amenable to Chlorination, Manual of Methods for Chemical Analysis of Water and Wastes, 1979." Statistical evaluation of the test results was obtained at several concentration levels. The following chapters present and discuss the development and evaluation of the analytical test procedures used in this study.

The EPA method referred to is actually a modification of the approved procedure. Among the modifications described on page 17, paragraph 4.4.1, is the use of an electrode finish instead of the titrimetric and colorimetric finishes. The modified method is presented in Appendix E.

SECTION 2

CONCLUSIONS

A number of analytical test procedures for the analysis of total cyanides, simple cyanides, and thiocyanates in water samples have been developed and/or evaluated. The operating characteristics of each of these methods are summarized below.

- Total Cyanides

  High Temperature Distillation--The primary advantage of this procedure is its ability to recover cyanide from all of the compounds studied, including the thermodynamically stable, kinetically inert $K_3[Co(CN)_6]$. The method is subject to a number of interferences including sulfide and thiocyanate. The lower limit of detection using this method is estimated to be 6 ppb, higher than any of the other total cyanide methods studied.

  EPA Total Cyanides-- A modification of the procedure used by the EPA for the analysis of total cyanides was evaluated. Complete recoveries of cyanide were possible from all of the compounds studied except $K_3[Co(CN)_6]$. Included in this list are the stable ferri- and ferrocyanide complexes. The lower limit of detection is 2 ppb ± 1 ppb. The relative standard deviation above 10 ppb is less than ±10%. The main disadvantage of the procedure is interference from a number of compounds. Of major concern are sulfide and thiocyanate. Various procedures have been described to alleviate these problems, but these procedures also introduce additional problems. As such, this method should be used for the analysis of cyanide in samples that do not contain either sulfide or thiocyanates.

  Ligand-Exchange--A procedure was developed that gives not only complete recovery of cyanide from all of the compounds studied except $K_3[Co(CN)_6]$, but also is unaffected by the presence of either sulfide or thiocyanate. This is a major development in the field of cyanide analysis, since these compounds have historically been a major problem. Another advantage is a 30% reduction in analysis time. The lower limit of detection is 2 ppb ± 1 ppb. The relative standard deviation above 10 ppb is less than ±10%.

- Simple Cyanides

  Ion Exchange--An ion exchange procedure for the analysis of simple cyanides was evaluated and found to be unacceptable. Among its deficiencies are: (1) the lower limit of detection is well above 2 ppm, (2) analyses are time consuming, and (3) there is incomplete recovery of cyanide from the column during the rinsing operations. Only considerable developmental effort could improve the performance of this procedure.

EDTA Electrode--Although this is a relatively simple procedure, its use is limited only to samples that do not contain certain other interfering compounds. The procedure is able to accurately measure only easily dissociable cyanides. Only with additional developmental work could this procedure be made to operate efficiently.

Continuous-Flow Distillation--Although this procedure is fast and easy to operate, the iron cyanides are partially decomposed, which leads to spuriously high results. A vast amount of additional work is required to improve the performance of this method. However, this procedure could be adapted for use as an analytical method for total cyanides.

AISI Aeration--The major disadvantage of this procedure is its inability to obtain complete recoveries from the cyanides equivalent to cyanides amenable to chlorination. Also of concern are its increased lower limit of detection (5 ppb) and lower precision. These problems are inherent in the technical design of the apparatus and could probably be improved through modifications of the apparatus and procedure.

EDTA Aeration--In an effort to take advantage of the beneficial characteristics of the preceding two methods, an EDTA-Aeration procedure was developed and evaluated. Incomplete recoveries of cyanide were found from half of the simple cyanides studied and a lower limit of detection of 5 ppb. Most significantly, neither thiocyanate nor sulfide (as PbS) interfere with an analysis.

EPA Procedure for Cyanides Amenable to Chlorination--The EPA procedure for chlorination and distillation of the samples has been evaluated in our laboratories. Incomplete recoveries of cyanide were found from a number of simple cyanide species. These recoveries are also concentration dependent. Recoveries could probably be improved by altering the chlorination conditions. The lower limit of detection is 2 ppb ± 1 ppb. Since the method relies on the EPA modified total cyanide methodology, all of the deficiencies associated with that method are also applicable here. Because of its widespread use, additional effort should be expended to improve the method.

Modified Roberts-Jackson--Incomplete recovery of cyanide is found only from the mercury-cyanide compounds. The addition of chloride ion during analysis will probably overcome this deficiency. The procedure is unaffected by the presence of either sulfide or thiocyanate. Other compounds that interfere are removed before analysis. A lower limit of 2 ppb ± 1 ppb is possible with a precision of ±10% above 10 ppb.

- Thiocyanates

Three different analytical techniques for the analysis of thiocyante have been investigated--colorimetry, high performance liquid chromatography, and atomic absorption spectroscopy. All three methods rely on the formation of a mixed ligand complex between copper(II), pyridine, and thiocyanate. The complex is normally extracted into chloroform, at which point problems develop. At concentrations below 200 ppb, the high background level of copper interferes with detection of thiocyanate. Thus, even though the analytical methods are quite sensitive, the effective lower limit of detection of thiocyanate is over 100 ppb.

SECTION 3

RECOMMENDATIONS

The following recommendations are made for the analysis of simple cyanides, total cyanides, and thiocyanates.

(1) Developmental work on the ligand-exchange method for analysis of total cyanide should be continued. In particular, the conditions of analysis should be improved and this optimized procedure should be ruggedized and evaluated on both laboratory standards and field samples.

(2) If the analysis of those metal-cyanide complexes more stable than either ferri- or ferrocyanide is needed, additional effort should be expended on the development of the high temperature distillation.

(3) Performance of the Roberts-Jackson method of analysis could be improved with minor modification. A comprehensive evaluation of the method should be conducted to determine the effect of chloride ion on cyanide recoveries and interferences. On this basis, a procedure should be optimized and evaluated on laboratory-prepared samples.

(4) Recoveries from the EPA procedure "Cyanides Amenable to Chlorination" might be improved by modifying the chlorination procedure. A study should be undertaken to determine the most efficient chlorination conditions and a modified procedure should be developed.

(5) We feel that the lower limits of detection for cyanide could be lowered by one order of magnitude by adjusting the pH of the solution in the electrode finish. The optimum pH should be determined and then used in all the electrode procedures.

(6) To accurately assess the performance of the more effective total cyanide and simple cyanide methods, it is necessary to conduct a limited sampling and analysis schedule of industrial effluents. The sites selected for monitoring should represent widely divergent sources and include sites where cyanide and common interferences are expected. Some sites that should be sampled include refineries, coking operations, and coal gasification industries.

(7) The methods evaluated for thiocyanate analysis are unsatisfactory. A number of recommendations, too numerous to mention here, are given in Section 6.5.

SECTION 4

TOTAL CYANIDE METHODOLOGY

4.1 INTRODUCTION

Total cyanide refers to all of the CN^- groups in a sample regardless of the metal complex, if any, with which the CN^- is associated. There is wide variation between the chemical characteristics of the different metal-cyanide complexes included in this study. This variation is readily apparent in Tables 4.1 and 4.2, which list thermodynamic constants of some of these metal-cyanide complexes. An ideal method of analysis for total cyanide should assess cyanide levels in a sample regardless of the metal-cyanide compounds making up this sample, as well as minimize the effects of interferences.

TABLE 4.1 SOLUBILITIES OF METAL-CYANIDE COMPOUNDS

Compound	Name	Solubility (mole/L)
$AgCN$	Silver cyanide	1.64×10^{-6} (20°C)[a]
$Cd(CN)_2$	Cadmium cyanide	1.51×10^{-5} (18°C)[a]
$Co(CN)_2$	Cobaltous cyanide	3.77×10^{-4} (18°C)[a]
$Cu(CN)$	Cuprous cyanide	2.90×10^{-5} (18°C)[a]
$Fe(CN)_2$	Ferrous cyanide	---
$Fe(CN)_3$	Ferric cyanide	---
$Hg(CN)_2$	Mercuric cyanide	3.68×10^{-1} (20°C)[a]
$Hg_2(CN)_2$	Mercurous cyanide	1.79×10^{-6} (25°C)[a]
$Mn(CN)_2$	Manganous cyanide	---
$Ni(CN)_2$	Nickel cyanide	5.35×10^{-4} (18°C)[a]
$Zn(CN)_2$	Zinc cyanide	4.90×10^{-5} (18°C)[a]
$K[Ag(CN)_2]$	Potassium dicyanoargentate(I)	1.3 (20°C)[b]
$K_2[Cd(CN)_4]$	Potassium tetracyanocadmate(II)	1.1[b]
$K_3[Cr(CN)_6]$	Potassium hexacyanochromate(III)	1 (20°C)[b]
$K_3[Fe(CN)_6]$	Potassium hexacyanoferrate (III) (Ferricyanide)	1 (4°C)[b]
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate (II) (Ferrocyanide)	0.7 (12°C)[b]

[a] Reference 1.
[b] Reference 2.

TABLE 4.2 STABILITY CONSTANTS OF METAL-CYANIDE COMPOUNDS

Complex	Name	Log Stability constant at 25°C
$K_4[Mn(CN)_6]$	Potassium hexacyanomanganate(II)	9.7[a]
$K_2[Zn(CN)_4]$	Potassium tetracyanozincate(II)	16.7[a]
$K_2[Cd(CN)_4]$	Potassium tetracyanocadmate(II)	16.9[a]
$K[Ag(CN)_2]$	Potassium dicyanoargentate (I)	20.9[b]
$K_3[Cu(CN)_4]$	Potassium tetracyanocuprate(I)	30.3[a]
$K_2[Ni(CN)_4]$	Potassium tetracyanonickelate (II)	31.3[a]
$K_2[Hg(CN)_4]$	Potassium tetracyanomercurate(II)	41.1[a]
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II) (Ferrocyanide)	47[a]
$K_3[Fe(CN)_6]$	Potassium hexacyanoferrate (III) (Ferricyanide)	52[a]
$K_3[Co(CN)_6]$	Potassium hexacyanocobaltate (III) (Cobalticyanide)	64[a]

[a] Reference 3.
[b] Reference 4.

Comprehensive laboratory evaluations were planned to determine how closely each method approached ideal behavior. The evaluations included studying the response of the procedure on ten simple, $M_1(CN)_x$, and six complex $M_1M_2(CN)_x$, cyanides. Solutions of these compounds were prepared in deionized water at four concentration levels; 2, 20, 200, and 2000 ppb CN^-. The ferrous, ferric and manganous cyanides, which are not stable as isolated salts, were prepared in solution from potassium cyanide and the appropriate metal chloride or sulfate. The effect of interferences at two levels for each interference was studied. The interferences are listed in Table 4.3. If, during preliminary investigations, a procedure was found to exhibit numerous deficiencies, further work on that procedure was curtailed.

TABLE 4.3 COMPOUNDS STUDIED AS POTENTIAL INTERFERENCES

$Ca(OCl)_2$
$NaNO_2$
NH_4Cl
MnO_2
$CH_3CH_2CH_2CHO$
Na_2S
$CH_3CH_2CH_2CH_2SCN$
$KOCN$
$KSCN$
$Co(SCN)_2$
$K_2[Hg(SCN)_4]$
$K_3[Co(SCN)_6]$

The methods developed and evaluated were manual methods useful for the analysis of water and wastewater samples. The methods have sensitivities of less than or equal to 2 ppb CN with a precision of ±1 ppb in the range of 2 to 10 ppb and ±10% above 10 ppb CN.

This section describes the results of the evaluations conducted in our laboratory.

4.2 HIGH TEMPERATURE DISTILLATION

4.2.1 Introduction and Background

The conventional reflux distillation procedures[5-7] for the analysis of total cyanides have gained wide acceptance, but they are not able to achieve complete recovery of cyanide from the more stable cyanide complexes. For instance, use of the analytical procedure currently recommended by the Environmental Protection Agency[5] gives only a 10% recovery of cyanide from hexacyano cobaltate(III). To improve recoveries of cyanide from these highly stable and kinetically inert cyanide compounds, a number of approaches have been devised. These approaches include fusion with potassium in a nickel bomb,[8] the Carius sealed tube method,[9] decomposition at elevated temperatures in a stream of hydrogen,[10] photodecomposition,[11] and high temperature distillations.[12],[13] A procedure based on this last concept was developed for the determination of total cyanide.

4.2.2 Procedure

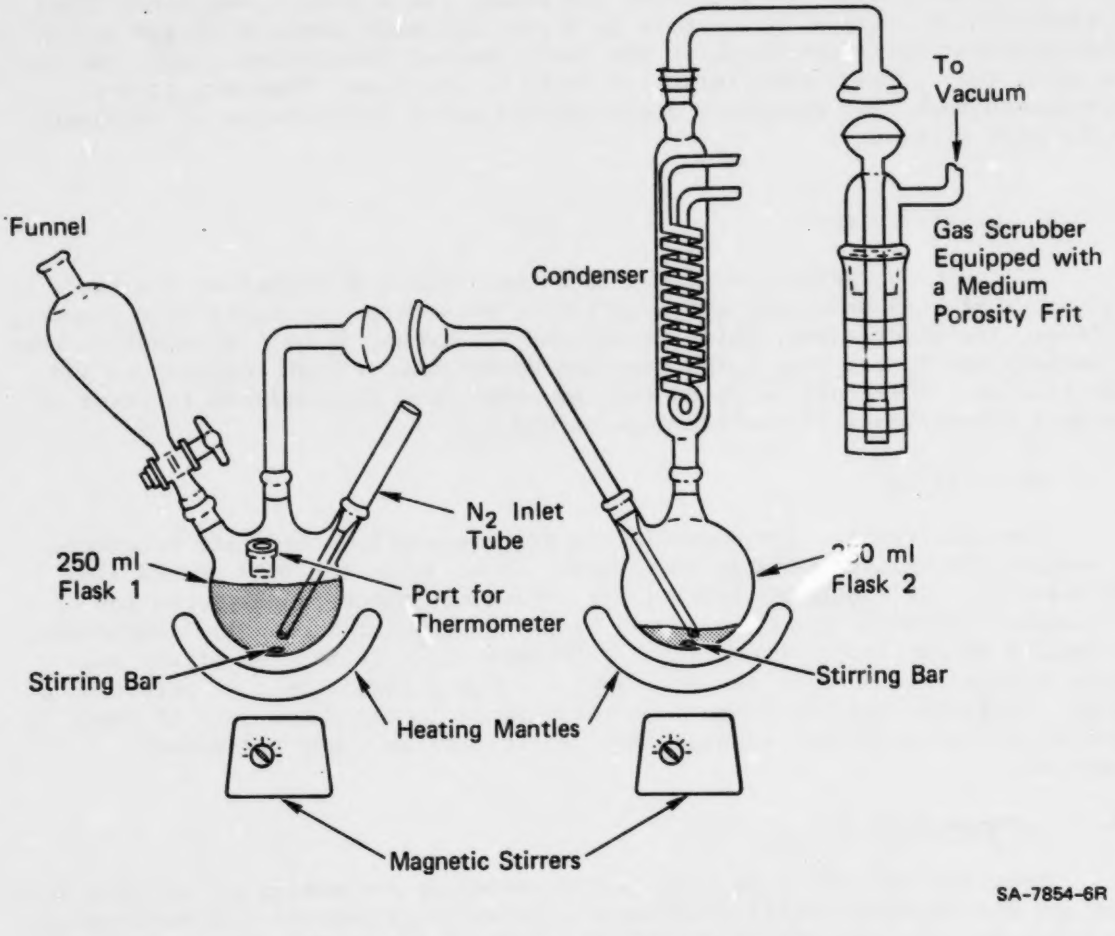
After much development work, a procedure was standardized that was subsequently used in all further laboratory evaluations. The apparatus developed is depicted in Figure 4.1. Briefly, the procedure is as follows. The funnel is charged with 60 mL of an aqueous mixture of 50% (by volume) of 85% orthophosphoric acid and 4% (by volume) of 50% hypophosphorous acid. To flask 2 is added 2 mL of 85% orthophosphoric acid and enough water to cover the tip of the inlet tube. To flask 1 is added 100 mL of sample or an aliquot diluted to 100 mL The gas scrubber is charged with 10 mL of 1.25 N sodium hydroxide and enough water to give an adequate depth of liquid. The apparatus is assembled as diagrammed and a stream of nitrogen is pulled through the reaction flask at a flow rate of approximately 4 bubbles per second. After dropwise addition of the acid mixture to the reaction flask, both flasks are heated to boiling.

As the water from flask 1 is removed, the temperature in the flask rises to 170°C, where it is maintained for 15 minutes. The heating of flask 1 is discontinued after this time, and the nitrogen flow is allowed to continue for an additional 15 minutes. The contents of the scrubber are then quantitatively transferred to a 50-mL volumetric flask, and this solution is analyzed for cyanide.

4.2.3 Results and Discussion

4.2.3.1 Cyanide Recoveries--

Complete recovery of cyanide from KCN, $K_3Fe(CN)_6$, and $K_3Co(CN)_6$ was possible using this procedure. Although the high temperature distillation procedure is adequate for the analysis of cyanide from these more stable complexes, it does have limitations, For example, when this procedure was designed, the intension was to use the $Ag^+/S^=$ ion-selective electrode for the analysis of the liberated cyanide. It has been reported by others[10] that cyanide could be detected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Condenser
N$_2$ Inlet Tube
250 ml Flask 1
Port for Thermometer
250 ml Flask 2
Stirring Bar
Stirring Bar
Heating Mantles
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SA-7854-6R

Figure 4.1 High temperature distillation apparatus.

down to 1 ppb using this technique. Replication of their work was possible with similar results (see Figure 4.2). However, during our investigations, it was found that when analyzing a series of unknowns of random concentrations, the electrode does not respond in the manner depicted by the calibration curve. Because of the slow exchange rate of cyanide for the anions that make up the pellet of the electrode, and the resulting carryover of cyanide from one solution to the next, it was not possible to analyze cyanide solutions with any degree of confidence. Also, the equilibration time required to attain a stable voltage reading was often in excess of 15 minutes.

For these reasons use of this electrode was abandoned in favor of the less sensitive cyanide ion-selective electrode. As a result, the lower limit of detection of cyanide in a sample is 6 ppb, slightly above the 2 ppb method development criteria set forth by the Environmental Protection Agency. By redesigning the system, this limitation could be overcome. However, it was anticipated that this procedure would exhibit other deficiencies as outlined in the next section.

4.2.3.2 Interferences--

A major disadvantage of the high temperature distillation procedure is the number of compounds that are expected to interfere, including thiocyanates, sulfides, organic thiocyanates, fatty acids, and aldehydes, as well as others. This is largely due to the very harsh reaction conditions of high temperature and high acidity. Therefore, work on this procedure was discontinued in favor of the more advantageous ligand-exchange method.

4.2.4 Conclusions

The high temperature distillation procedure allows complete recoveries of cyanide from all the stable complexes. Thus, it is the only method that can quantitate CN^- bound to cobalt(III). However, since the dissociation of the cobalt compounds is achieved only by using very harsh reaction conditions, the method is subject to a number of interferences. It is also likely that longer analysis times will be necessary to reach a lower limit of detection of 2 ppb. Thus, further development of this method is warranted only if there is a definite need to detect cyanide from cobalt(III) or other refractory compounds.

4.2.5 Recommendations

Modifications could be made to the procedure and design of the high temperature distillation method that would substantially improve its performance. For instance, if a moderately acidified solution of a lead, cadmium, or arsenic salt were substituted for the solution currently used in the second flask, the interferences from sulfide and thiocyanate could probably be eliminated. Additional developmental work in this area should yield a procedure for the analysis of total cyanide that is capable of quantitating all types of cyanide compounds from a wide variety of sample matrices.

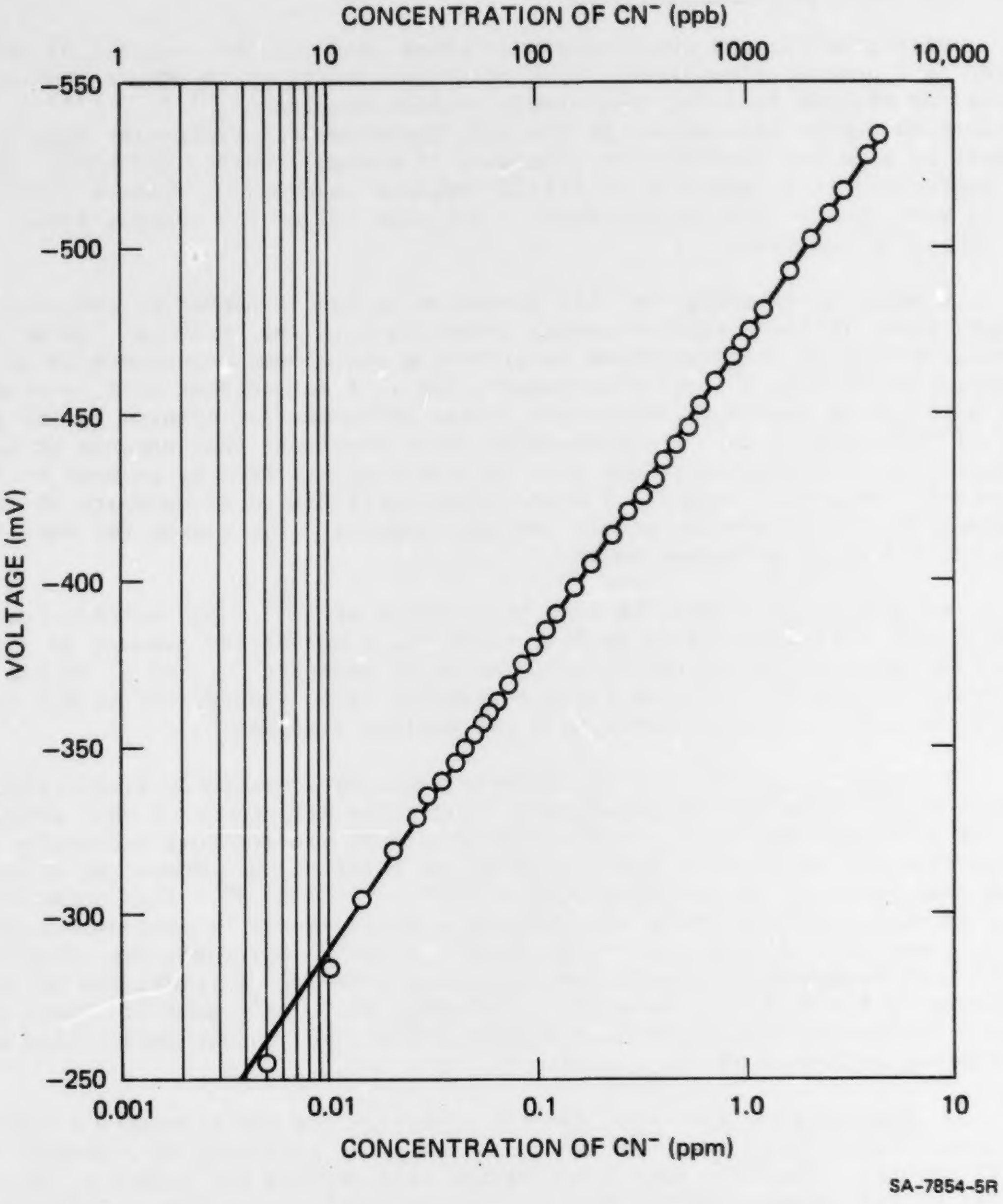


Figure 4.2 Emf response of Orion's 94-16A $Ag^+/S^=$ ion selective electrode as a function of CN^- concentration.

4.3 LIGAND-EXCHANGE TOTAL CYANIDE METHOD

4.3.1 Introduction and Background

Historically, the procedures most often used for the analysis of total cyanide have generally employed harsh reaction conditions to ensure complete recovery of cyanide from the more stable cyanide complexes.[5-8,10-12,14-18] The procedure currently recommended by the U.S. Environmental Protection Agency[5] consists of a reflux distillation procedure in a highly acidic solution. Using this procedure, it is possible to attain complete recovery of cyanide from all but the most stable cyanide complexes. Less than 15% of the cyanide from $K_3[Co(CN)_6]$ is recovered.

A major disadvantage of this procedure is that a number of compounds commonly found in industrial effluents interfere with the analysis. Of major concern, because of their positive interference and common occurrence in effluents, are sulfide, $S^=$, and thiocyanate, SCN^-. A method that will overcome these problems is needed to accurately assess effluents for cyanide in the presence of these compounds. A procedure has been developed that not only is less susceptible to interferences, but also reduces analysis time by as much as 30%. The method consists of a one-half hour reflux distillation at moderate pH in the presence of sequestering agents and lead acetate. The reason for each of these conditions is discussed below.

- Lead Acetate--This is used as a source of Pb^{++}. Any sulfide present in the sample will precipitate as PbS, which has a solubility product of 7×10^{-28}. Since this precipitate is stable in hot water at moderate pH, any $S^=$ in the sample remains in the distillation flask instead of being transferred as H_2S to the scrubber solution and interfering with the various finishes.

- Moderate pH--The PbS precipitate would be appreciably dissociated in strongly acidic solution, releasing H_2S. Thus, the efficiency of this procedure for trapping sulfide is dependent on obtaining satisfactory recoveries of cyanide from the very stable metal cyanides at moderate pH. Operating at moderate pH also prevents the decomposition of SCN^- to produce $S^=$. This normally occurs in highly acidic reflux distillation procedures and is responsible for the large positive interference often found for SCN^-. Moreover, the effectiveness of most sequestering agents increases at higher pH. However, the CN^- must be protonated for efficient aeration of HCN from the sample matrix. Thus, pH 4.5 is a compromise that allows aeration of HCN without unduly restricting the sequestering abilities of the ligands.

- Distillation Time--The distillation time for the procedure is one-half hour. Complete recovery of CN^- from some metal complexes is possible in only 15 minutes. The half-hour distillation time reduced the extent of decomposition of PbS compared to the normal one-hour distillation time. This distillation time has the added advantage of substantially reducing the analysis time.

- Sequestering Agents--The ligands are used to aid decomposition of the cyanide complexes by a ligand-exchange reaction. This displacement can generally be depicted by the equation:

$$M(CN)_n + yL = M(L)_y + nCN^- \qquad (1)$$

Because the pH is well below the pKa of CN^-, the cyanide so liberated is quickly transferred as HCN to the sodium hydroxide scrubber solution. The use of a ligand to displace cyanide from the inner coordination sphere of a metal is not a new idea. Various procedures for the analysis of simple cyanides that make use of EDTA and an ion-selective electrode have been reported.[19-21] These methods are entirely unsuited for total cyanide analysis. A procedure for the analysis of total cyanide that makes use of EDTA has been described.[18] However, under the extremely acidic pH conditions employed in this procedure, EDTA is largely ineffectual at displacing cyanide. The reported success with this procedure is no doubt due to the increased distillation temperatures.

It was assumed that complete cyanide recovery would be most difficult to obtain from the iron, mercury, and cobalt(III) cyanides, since these complexes have the largest stability constants. Thus a successful ligand must form very stable complexes with these metal ions. However, the ligand should not strongly sequester lead, as this would have two detrimental effects. One, the formation of a lead complex would reduce the effectiveness of the ligand toward displacing cyanide from other metals. Two, if the complexation of lead is too strong, the ligand will displace $S^=$ and reduce the protection against this interference.

The stability constants of several ligands are listed in Table 4.4 Initial results showed that EDTA, EGTA, and CDTA all gave complete recovery of CN^- from the iron and mercury cyanides. However, they also increased the interference from sulfide. Thus a more selective ligand was needed. Tiron has an extremely high selectivity for Fe^{3+}, and the addition of tiron to the samples results in complete recovery of CN^- from both ferro- and ferricyanide, but only 60% recovery from $Hg(CN)_4^{2-}$.

TABLE 4.4 LOGARITHMS OF THE STABILITY CONSTANTS OF CATIONS WITH VARIOUS LIGANDS

Ligand	Hg^{2+}	Cd^{2+}	Pb^{2+}	Fe^{2+}	Fe^{3+}	Co^{3+}
CN^-	41	--	--	47	52	64
EDTA[a]	21.5	16.4	18	14.3	25.1	41.4
EGTA[b]	22.9	16.5	14.5	11.8	20.5	--
CDTA[c]	24.8	19.8	20.4	18.9	30.0	--
TEP[d]	27.7	14	10.5	9.9	--	--
Tiron[e]	19.1(1:1)[f]	13.3(2:1)[f]	15(2:1)[f]	--	45(3:1)[f]	--
$S^=$(Ksp)		28	29			

[a] Ethylenediamine-N,N,N',N'-tetraacetic acid

[b] 2,2'-Oxybis[ethyliminodi(acetic acid)]

[c] trans-Cyclohexane-1,2-diamine-N,N,N',N'-tetra-acetic acid

[d] Tetraethylenepentamine (3,6,9-triazaundecane,1,11-diamine)

[e] 1,2- dihydroxy-3,5-benzenedisulfonic acid

[f] Numbers in parentheses indicate ligand:metal ratio of tiron complex.

TABLE 4.5 CYANIDE RECOVERIES USING THE LIGAND EXCHANGE METHOD

	Concentration of CN^-								
	0.002 ppm			0.2 ppm			2 ppm		
Compound Studied	n	Mean Recovery (%)	Relative Standard Deviation (%)	n	Mean Recovery (%)	Relative Standard Deviation (%)	n	Mean Recovery (%)	Relative Standard Deviation (%)
KCN	6	120	21	4	98	4	4	100	1
$Cd(CN)_2$		-		4	101	2	4	100	1
Cu(CN)		-		4	99	1	4	100	1
$Ni(CN)_2$		-		4	99	1	4	99	2
$Hg(CN)_2$	2	115	-	4	99	2	4	98	2
$K_3[Cu(CN)_4]$	2	124	-	4	99	1	4	100	1
$K_2[Ni(CN)_4]$	2	119	-	4	105	3	4	102	2
$K_2[Hg(CN)_4]$	2	147	-	4	99	2	4	99	1
$K_4[Fe(CN)_6]$	2	147	-	4	104	3	4	101	2
$K_3[Fe(CN)_6]$	2	132	-	4	104	3	4	101	1
$K_3[Co(CN)_6]$		-		4	0	4	4	0	1

Note: n = Number of replicate analyses.

The stability constants in Table 4.4 show that TEP has a very high affinity for Hg^{2+}. Therefore, a mixture of both tiron and TEP was chosen for use. This procedure is described in Appendix D.

Cadmium ion was also evaluated as a sulfide precipitating reagent, but was less effective than Pb^{2+}. Since the Ksp values of CdS and PbS are comparable, the difference in effectiveness presumably is due to the much higher stability constant of 10^{14} of the cadmium-TEP complex compared with only $10^{10.5}$ for the Pb^{2+} complex. It appears that TEP can displace significant amounts of $S^=$ from cadmium, whereas the lead sulfide species is stable in the presence of TEP.

4.3.2 Results and Discussion

4.3.2.1 Cyanide Recovery--

An abbreviated study of the ligand-exchange method was conducted in the laboratory, and the results are shown in Table 4.5. This table includes mean recoveries and their standard deviations. It can be seen from these results that complete recovery of cyanide is obtained from each of the compounds investigated except $K_3[Co(CN)_6]$. There is essentially no cyanide recovered from this compound. Since recoveries from other procedures[5-7] are concentration dependent and do not normally exceed 15%, the lack of cyanide recovery from this complex is not a major disadvantage.

The lower limit of detection of the ligand-exchange method is 2 ppb. The method demonstrates precision within the guidelines outlined by the contract; that is, ±10% above 10 ppb cyanide and ±1 ppb in the range between 0-10 ppb. Thus the performance of the method with respect to recovery of cyanide from the various compounds meets the EPA standards as outlined.

4.3.2.2 Interferences--

The performance of the ligand-exchange in the presence of suspected interferences was also investigated. The results are depicted in Table 4.6.

TABLE 4.6 EFFECTS OF POTENTIAL INTERFERENCES ON CYANIDE RECOVERIES USING THE LIGAND-EXCHANGE PROCEDURE WITH AN ION SELECTIVE ELECTRODE FINISH

Compound	level mole interference:mole CN	Apparent recovery from KCN percent
$S^=$ (as Na_2S)	100:1	96
	10:1	102
	1:1	100
SCN^- (as KSCN)	100:1	101
NH_4^+ (as NH_4Cl)	1000:1	100
Butanal	1000:1	117

From these results, it is apparent that the method overcomes the problems normally associated with the presence of sulfide and thiocyanate. Unfortunately, the comprehensive evaluation of suspected interferences was not completed. However, on the basis of our experience using this and other analytical methodology, the following statements can be made concerning likely interferences:

Chlorine - Chlorine can be expected to cause a negative interference in a manner similar to that found in the other reflux distillation procedures investigated. This can be eliminated by proper sample pretreatment.

Butylthiocyanate - This can be expected to interfere in a positive manner when using the electrode finish. The compound exhibits a large vapor pressure at room temperature and would be expected to distill over using the procedure outlined and subsequently interfere with the ion-selective electrode. It may also interfere with the colorimetric and titrimetric finishes by its production of a translucent scrubber solution. This can probably be eliminated by using the extraction procedure outlined for removing fatty acids.

Aldehydes - Aldehydes are expected to interfere because of their reaction with cyanide to form cyanohydrins and further hydrolysis to the corresponding acid and ammonia. In some instances, this compound can be removed by the fatty acid extraction procedure. In addition, the presence of the amine ligand TEP offers considerable protection.

Fatty Acids - If the colorimetric finish is used, these compounds are expected to interfere in a manner similar to that found for the generally accepted procedures.[5-7] However, the pH used in this method and the short analysis time should minimize this problem and obviate the need for the extraction procedure that has been described for removal of these compounds.

Other compounds commonly found in a sample that would be expected to interfere are eliminated by the distillation procedure.

4.3.3 Conclusions

A new method for the analysis of total cyanide that overcomes a number of problems normally associated with the generally accepted methods was developed and evaluated.[5-7] The procedure is simple and fast to operate, does not require any exotic equipment or chemicals, can be readily adapted for use on the equipment currently required by the approved method, and does not experience interferences from $S^=$ or SCN^-. As such, it should be able to accurately assess and monitor a wider variety of industrial effluents than was possible using other procedures.

4.3.4 Recommendations

Further work should be conducted to determine the optimum operating parameters of a method based on the ligand-exchange principle. Once this optimized procedure has been developed, a comprehensive evaluation should be conducted including ruggedness and round robin tests. This evaluation should consist of determining the performance of the method on laboratory-prepared samples of a number of compounds at various concentrations, the effect of suspected interferences on the procedure, and the applicability of the method for monitoring industrial effluents. It should also include a side-by-side comparison of this method with the procedure recommended for use by the EPA.

4.4 EPA TOTAL CYANIDE METHOD

4.4.1 Introduction and Background

Briefly stated, the EPA procedure is a one-hour catalytic reflux distillation procedure operated at a low pH. The cyanide compounds present in the sample are dissociated and the cyanide, as hydrocyannic acid (HCN), is transferred to a sodium hydroxide scrubber solution. This solution is then quantitatively transferred to a volumetric flask and subsequently analyzed for cyanide using either a titrimetric or colorimetric finish. A procedure that is closely allied to that procedure recommended by the U.S. Environmental Protection Agency for the analysis of total cyanides was evaluated. The modifications to the EPA method consist of the following: (1) addition of boiling chips to the distillation flask, (2) transferring the scrubber solution to a smaller volumetric flask, and (3) the use of an ion-selective electrode finish rather than a colorimetric or titrimetric finishes. (Refer to Appendix E for the description of the procedure used.)

4.4.2 Results and Discussion

4.4.2.1 Cyanide Recoveries--

The performance of this method with respect to cyanide recoveries on a number of compounds at each of four concentration levels (2, 20, 200, and 2000 ppb) was evaluated. The results of this extensive investigation are depicted in Table 4.7. This table includes several statistical parameters, including the number of analyses performed, mean recoveries, and relative standard deviations. It is apparent from these results that the procedure is more than adequate on laboratory-prepared samples.

Only partial recovery of cyanide from $K_3[Co(CN)_6]$ was found. The reason for this is no doubt the slow kinetics of the decomposition of this complex. At the pH used in the analysis, the decomposition of the complex is thermodynamically favored. Since this complex may not be found in many industrial effluents, incomplete recovery of cyanide from this compound may not be a major problem.

From the results in Table 4.7, it is also apparent that there is no recovery of cyanide from the nitriles. This is not an unexpected result. Under the analysis conditions, these compounds can be expected to hydrolyze to their corresponding acids as depicted below:

$$R\text{-}C\equiv N + H_2O \xrightarrow{H^+} RCOOH + NH_4^+$$

TABLE 4.7 CYANIDE RECOVERIES OBTAINED WITH THE EPA TOTAL CYANIDE METHOD USING AN ION-SELECTIVE ELECTRODE FINISH

	Concentration of CN^-											
	0.002 ppm			0.02 ppm			0.2 ppm			2 ppm		
Compound Studied	n	Mean Recovery (%)	Relative Standard Deviation (%)	n	Mean Recovery (%)	Relative Standard Deviation (%)	n	Mean Recovery (%)	Relative Standard Deviation (%)	n	Mean Recovery (%)	Relative Standard Deviation (%)
Simple Cyanides												
KCN	6	87	8	6	99	2	6	100	0.5	6	100	0.5
$Cd(CN)_2$	4	48	20	4	101	1	4	102	3	4	99	0.5
$Co(CN)_2$	4	127	28	4	65	3	4	35	6	4	32	5
CuCN	2	92	-	2	99	-	2	94	-	2	98	-
$Fe(CN)_2$	2	96	-	2	100	-	2	100	-	2	110	-
$Fe(CN)_3$	2	96	-	2	100	-	2	100	-	2	100	-
$Hg(CN)_2$	4	73	63	4	99	0.5	4	100	2.8	4	100	0.5
$Mn(CN)_2$	2	100	-	2	100	-	2	100	-	2	99	-
$Ni(CN)_2$	4	101	17	4	97	2.4	4	98	2.4	4	99	1.1
$Zn(CN)_2$	2	76	-	2	99	-	2	100	-	2	105	-
Complex Cyanides												
$K_3[Cu(CN)_4]$	6	130	104	6	96	7.8	6	97	3.4	6	101	4
$K_4[Fe(CN)_6]$	6	105	7.9	6	101	4.2	6	104	4.7	6	99	3
$K_3[Fe(CN)_6]$	6	110	6	6	95	5	6	111	4.4	6	102	3
$K_2[Hg(CN)_4]$	4	25	215	4	99	0.6	4	99	0.5	4	99	1
$K_2[Ni(CN)_4]$	6	116	12	4	104	4	4	102	1.5	4	101	2.5
$K_3[Co(CN)_6]$	6	0	-	6	7	20	6	4	3	6	7	7
Organic Cyanides												
CH_3CN	6	0	-	6	0	-	6	0	-	6	0	1
$CH_3CH_2CH_2CN$	1	0	-	1	0	-	1	0	-	1	0	-

Note: n = number of replicate analyses.

Although one can expect to see nitriles in effluents, the inability of this procedure to detect these compounds is not of major concern, since these compounds are normally analyzed in effluents by other means.

4.4.2.2 Interferences--

The performance of this procedure was studied in the presence of a number of suspected interferences. The results of our investigation, given in Table 4.8, show that this procedure is sensitive to a number of interferences. These are discussed below.

Thiocyanate--All of the thiocyanate compounds interfere with the analysis. This interference can be attributed to the decomposition of SCN^- to form $S^=$, which is transferred to the scrubber solution as H_2S along with the HCN. The presence of sulfide in the scrubber solution was verified by visual observations of a yellow CdS precipitate upon treatment of the scrubber with a cadmium sulfate solution. The decomposition of SCN^- does not proceed rapidly, but occurs during the entire course of distillation. Hydrogen sulfide could still be detected in the reaction flask after the analysis was complete. This decomposition of thiocyanate to sulfide during distillation represents a major interference. The presence of sulfide in the distillate affects all three commonly used finishes: colorimetric, titrimetric, and potentiometric.

The sulfide can be removed from the distillate gas stream by placing another gas scrubber in the vacuum train ahead of the sodium hydroxide gas scrubber. The solution in this additional scrubber is acidified, pH 4.5, and contains lead acetate, to precipitate the sulfide.

A method that has been recommended for use in removing sulfide from the caustic scrubber solution is precipitation as the cadmium or lead salt, followed by filtration, which should produce a solution relatively free of sulfide. However, this procedure has been shown to adversely affect cyanide quantitation.[15]

Both of the above sulfide removal procedures add to the difficulty in performing an analysis and exhibit still other problems.

Sulfide--Sulfide present in the sample will be distilled as H_2S during the analysis and will contaminate the sodium hydroxide scrubber solution. As mentioned earlier, the sulfide can be removed from the sample solution by precipitation as the insoluble cadmium or lead salt followed by filtration. However, filtration also removes insoluble cyanides from the sample, and as a result, the actual cyanide content of the sample may be underestimated. Since the majority of cyanide compounds display rather small solubility products, this can be a serious problem.

Aldehyde--Aldehydes in the sample react with cyanide to form cyanohydrins, which are subsequently hydrolyzed to the corresponding acid and ammonia, thereby lowering the cyanide concentration. The procedure outlined for the removal of fatty acids will also remove a number of aldehydes. However, the problem cannot be completely alleviated by this procedure.

TABLE 4.8 EFFECTS OF POTENTIAL INTERFERENCES ON CYANIDE RECOVERIES OBTAINED WITH THE EPA TOTAL CYANIDE METHOD WITH AN ION-SELECTIVE ELECTRODE FINISH

Potential Interference Compounds	Level of Interference Mole:Mole of CN^-	Apparent Recovery of Cyanide (%) from Designated Compound				
		KCN	CuCN	$Hg(CN)_2$	$K_3[Cu(CN)_4]$	$K_4[Fe(CN)_6]$
KSCN	100:1	19000	19000	16000	28000	36000
	1:1	160	120	210	120	450
$Co(SCN)_2$	100:1	32000	19000	28000	24400	40000
	1:1	170	110	260	125	600
$K_2[Hg(SCN)_4]$	100:1	23000	-	34000	-	-
	1:1	330	-	380	-	-
$K_3[Co(SCN)_6]$	100:1	100000	-	94000	-	-
	1:1	360	-	710	-	-
n-butylthiocyanate	100:1	5800	-	5500	-	-
	1:1	170	-	180	-	-
OCN^- (as KOCN)	100:1	100	100	100	105	105
	1:1	-	-	-	-	-
NH_4^+ (as NH_4Cl)	100:1	99	98	100	110	100
	1:1	-	-	-	-	-
MnO_2	100:1	100	100	100	110	105
	1:1	-	-	-	-	-
Butanal	100:1	60	98	100	88	100
	1:1	92	-	-	105	-
$S^=$ (as Na_2S)	10:1	2800	4700	3400	3800	3600
	1:1	250	240	190	185	180
Cl_2 (as $Ca(OCl)_2$)	10:1	0	0	0	0	0
	1:1	0	0	0	0	0
NO_2^- (as $NaNO_2$)	100:1	100	97	100	110	99
	1:1	-	-	-	-	-

Note: Cyanide concentration level was 0.2 ppm in all test solutions.

Chlorine--Chlorine present in a sample will oxidize cyanide in the sample and produce abnormally low results. The procedure recommended for removing excess chlorine is the incremental addition of ascorbic acid. Although this procedure is effective in reducing the Cl_2 content, an excess of ascorbic acid will produce a yellow scrubber solution, thus interfering with the colorimetric finish. The ion-selective electrode's response remains unaffected.

Butylthiocyanate--This compound, if present in the sample, will distill during an analysis. It interferes with both the colorimetric and electrode finishes (the former by production of a cloudy scrubber solution). Because of the limited solubility of this compound in water, it appears that the extraction method recommended for removing fatty acids will also remove it.

Fatty Acids--Because of their finite vapor pressure under the analysis conditions, fatty acids are distilled over into the caustic scrubber solution, where they saponify and produce a cloudy solution. This interferes with the colorimetric but not the potentiometric finish. An extraction procedure has been recommended for use to remove these substances.

4.4.3 Conclusions

The EPA total cyanide procedure is well suited for the analysis of samples not containing the above constituents. The procedure gives complete recovery of cyanide from all of the compounds studied except $K_3[Co(CN)_6]$. The lower limit of detection is 2 ppb. A major difficulty appears to be the large number of compounds that interfere with the method. Thus a need exists for the development of an analytical technique that can accurately assess cyanide levels in other than clean samples.

This need is most accurately demonstrated by industrial effluents from energy related industries. Refineries, coking operations, and coal gasification industries produce effluents that can be expected to have high levels of not only cyanide, but also thiocyanate and sulfide. (In view of the recent expansion of the syn-fuel program, this need becomes most acute.) The total cyanide procedure is inadequate for analyzing samples from such sources.

4.4.4 Recommendations

Barring any new improvements in this method, it is recommended that the use of this procedure be restricted to samples not containing the above constituents; most notably sulfide and thiocyanate. It is also recommended that development and evaluation be continued on the alternative procedure described in Section 4.2 for the analysis of samples for total cyanide, as it appears to be most advantageous.

4.5 COMPARISON AND SUMMARY OF TOTAL CYANIDE METHODOLOGY

Of the two methods that have been evaluated in the most depth, the ligand-exchange and catalytic reflux distillation procedures, both behave in a comparable manner with respect to cyanide recoveries. Both procedures give complete recoveries of cyanide from all of the compounds studied except $K_3[Co(CN)_6]$ (See Table 4.9).

Both procedures also meet the criteria as set forth in the contract for precision, accuracy, and sensitivity. The lower limit of detection for both procedures is 2 ppb. In the range between 0-10 ppb, the precision is ±1 ppb. Above 10 ppb, the precision is within ±10%. (See Tables 4.5 and 4.7).

A comparison of their performance with respect to interferences reveals that the ligand-exchange procedure outperforms the catalytic reflux distillation method. This is most accurately depicted in Table 4.10. It can be seen from this table that thiocyanate and sulfide interfere with the catalytic reflux distillation procedure but not the ligand-exchange procedure. Since these anions are common pollutants, this represents a significant improvement in total cyanide analysis.

Another advantage of the ligand-exchange method is its ability to reduce analysis time by approximately 30%. This will substantially reduce the cost of an analysis since the greatest expense incurred is that associated with labor.

TABLE 4.9 COMPARISON OF CYANIDE RECOVERIES OBTAINED WITH THE EPA AND LIGAND-EXCHANGE TOTAL CYANIDE PROCEDURES

	Concentration Level PPB CN			
	2000 ppb CN		200 ppb CN	
Cyanide Compound	EPA	Ligand exchange	EPA	Ligand exchange
KCN	Complete	Complete	Complete	Complete
$Cd(CN)_2$	Complete	Complete	Complete	Complete
CuCN	Complete	Complete	Complete	Complete
$Ni(CN)_2$	Complete	Complete	Complete	Complete
$Hg(CN)_2$	Complete	Complete	Complete	Complete
$K_3[Cu(CN)_4]$	Complete	Complete	Complete	Complete
$K_2[Ni(CN)_4]$	Complete	Complete	Complete	Complete
$K_2[Hg(CN)_4]$	Complete	Complete	Complete	Complete
$K_3[Fe(CN)_6]$	Complete	Complete	Complete	Complete
$K_4[Fe(CN)_6]$	Complete	Complete	Complete	Complete
$K_3[Co(CN)_6]$	Partial	None	Partial	None

TABLE 4.10 COMPARISON OF INTERFERENCES ON THE EPA AND THE LIGAND-EXCHANGE TOTAL CYANIDE PROCEDURES

Compounds studied for interference	Level Mole interference: mole CN^-	EPA total cyanide procedure	Ligand exchange procedure
SCN^- (as KSCN)	100:1	++	0
	1:1	+	
$S^=$ (as Na_2S)	100:1		0
	10:1	++	0
	1:1	++	0
Butanal	1000:1		0
	100:1	-	
	10:1	0	
NH_4^+ (as NH_4Cl)	1000:1	-	0
	100:1	0	
	10:1	0	

++ severe positive interference	- slight to moderate negative interference
+ slight to moderate positive interference	0 no interference

SECTION 5

SIMPLE CYANIDES METHODOLOGY

5.1 INTRODUCTION

Total cyanide has been used to indicate the sum of all the CN^- groups in a sample, regardless of the nature of the metal complex with which the CN^- is associated. A subset of total cyanide is a group of metal compounds commonly referred to as "simple cyanides." Despite the widespread use of this term, no single definition has gained complete acceptance. The term is intended to denote easily dissociable cyanide complexes, and is frequently used as a synonym for "cyanides amenable to chlorination." The definition used in this report is that from the contract statement of work--a definition based on the easily defined stoichiometry of the cyanide complexes. Thus, the neutral stoichiometric cyanides $[M^{n+}(CN)_n]$ are considered to be simple cyanides. The more highly associated salts that dissolve in aqueous solution to produce $[M^{n+}(CN)_y]^{(y-n)}$ anions are defined as complex cyanides. Table 5.1 lists the compounds included in this study.

TABLE 5.1 COMPOUNDS INCLUDED IN STUDY

Cyanide compound
KCN
$Cd(CN)_2$
$Co(CN)_2$
CuCN
$Fe(CN)_2$
$Fe(CN)_3$
$Hg(CN)_2$
$Mn(CN)_2$
$Ni(CN)_2$
$Zn(CN)_2$
$K_3[Cu(CN)_4]$
$K_2[Ni(CN)_4]$
$K_2[Hg(CN)_4]$

(continued)

TABLE 5.1

Cyanide compound
$K_3[Fe(CN)_6]$
$K_4[Fe(CN)_6]$
$K_3[Co(CN)_6]$

Six analytical methods for simple cyanides have been studied; two of these have been compared in detail with the EPA method, "Cyanides Amenable to Chlorination." (Strictly speaking, comparisons were made to a modified EPA procedure. The modifications used were: addition of boiling chips during distillation, smaller volumetric flasks, and an electrode finish. These modifications are included in the method as it appears in Appendix C.) This laboratory work generally consisted of evaluating the performance of the method on prepared standards of metal-cyanide compounds. The compounds studied included ten simple and six complex cyanides. These compounds were prepared in deionized water at four concentration levels. The effect of suspected interferences was also evaluated. Table 4.3 lists the substances studied for interferences.

In some instances, severe problems were identified early in the development phase. In these cases, only an abbreviated study was conducted. since further work on an inherently deficient method was deemed inappropriate.

5.2 ION EXCHANGE PROCEDURE

5.2.1 Introduction and Background

A procedure developed by Gilath[22] for the analysis of simple cyanides appeared to be fast, simple, and efficient. Complete recoveries of cyanide from $K_2[Zn(CN)_4]$, $K_2[Cd(CN)_4]$, $K_3[Cu(CN)_4]$, and $K[Ag(CN)_2]$ were reported. On the basis of these reported results and knowledge of the chemistry of the various cyanide compounds, this procedure was considered to be ideally suited for the analysis of simple cyanides.

The procedure is based on the absorption of cyanide ion on a strong anion exchanger, followed by elution of the absorbed species by an acidic solution. The cyanide so eluted is then quantitated by any of a variety of techniques.

5.2.2 Procedure

The apparatus is depicted in Figure 5.1. The column was packed with 5 g of the strong anion exchange resin, Amberlite IR-400. The column was then backwashed to free the bed of entrapped air pockets, classify the resin

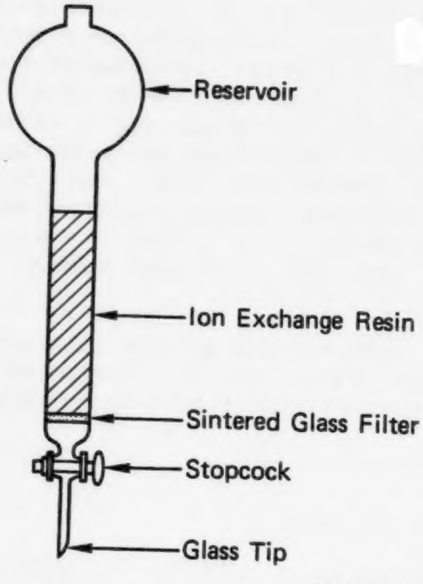

Reservoir
Ion Exchange Resin
Sintered Glass Filter
Stopcock
Glass Tip
SA-7854-11

Figure 5.1 Ion-exchange apparatus.

particles, and rid the bed of debris and resin fines. The resin was then converted to the hydroxide form and rinsed.

After preparation of the column, a 20-mL sample was allowed to flow through the resin bed at the rate of 1 drop/second. The column was then rinsed with 15 mL of distilled water at the same flow rates. The absorbed cyanide was then eluted from the column by two consecutive acid elutions. The first elution was performed with 15 mL of 2N H_2SO_4 and the second with 15 mL of 4.5N H_2SO_4. The first acid elution was performed quickly to avoid the loss of cyanide as HCN. The second acid wash was performed slowly in order to ensure complete removal of cyanide from the resin. The resin was then rinsed with 14 mL of distilled water. The acid eluents were delivered to a magnetically stirred beaker containing 80 mL of 2.05N sodium hydroxide. The delivery tip of the column was placed below the sodium hydroxide surface during the elutions to prevent loss of cyanide as HCN. The contents of this beaker were then quantitatively transferred to a volumetric flask and analyzed. The standards used for this analysis were prepared in solutions consisting of a similar matrix as that found in the sample.

5.2.3 Results and Discussion

Recovery of cyanide from a KCN standard was found to be only 25 ± 5%. These results differ significantly from those reported by Gilath.[22] Gilath conducted her studies on solutions containing between 21 and 40 g/L cyanide The concentrations of cyanide in the solutions analyzed in our investigation were approximately 1 mg/L. These levels are orders of magnitude lower than those used by Gilath. Apparently, the lower limit of detection of the method lies somewhere between 1 and 20,000 ppm. This lower limit is sufficiently high so that the method is not useful at the concentrations of major concern to us, namely between 2 and 2000 ppb.

Other shortcomings of a technical nature became apparent during our investigations. The procedure was found to be excessively time consuming. Several hours were required to regenerate and rinse the column in order to perform one analysis. There was some evidence of HCN evolution during the acid elution, resulting in abnormally low cyanide values. Finally, because of the low recoveries found, it would seem that some cyanide is still adsorbed on the resin. If so, this would impair the ability to use the column for more than one analysis.

Because of poor performance of the method during these initial investigations, further work using this method was discontinued.

5.2.4 Conclusions

The ion exchange method is deficient in several respects. Of major concern is the incomplete recovery of cyanide from a 2-ppm potassium cyanide sample. The method is also too time consuming for routine analyses because of the slow regeneration of the column.

5.2.5 Recommendations

In light of the performance of this procedure and that of the other procedures investigated in this laboratory, further work using the ion exchange method is inappropriate.

5.3 CONTINUOUS-FLOW DISTILLATION

5.3.1 Introduction and Background

An automated procedure designed by Goulden, Afghan, and Brooksbank[11] for the analysis of simple cyanides has been suitably altered for use as a manual method of analysis. The primary alterations to the system consist of replacing the pump-driven delivery systems with a gravity feed system and replacing the automated colorimetric finish with a manual potentiometric finish.

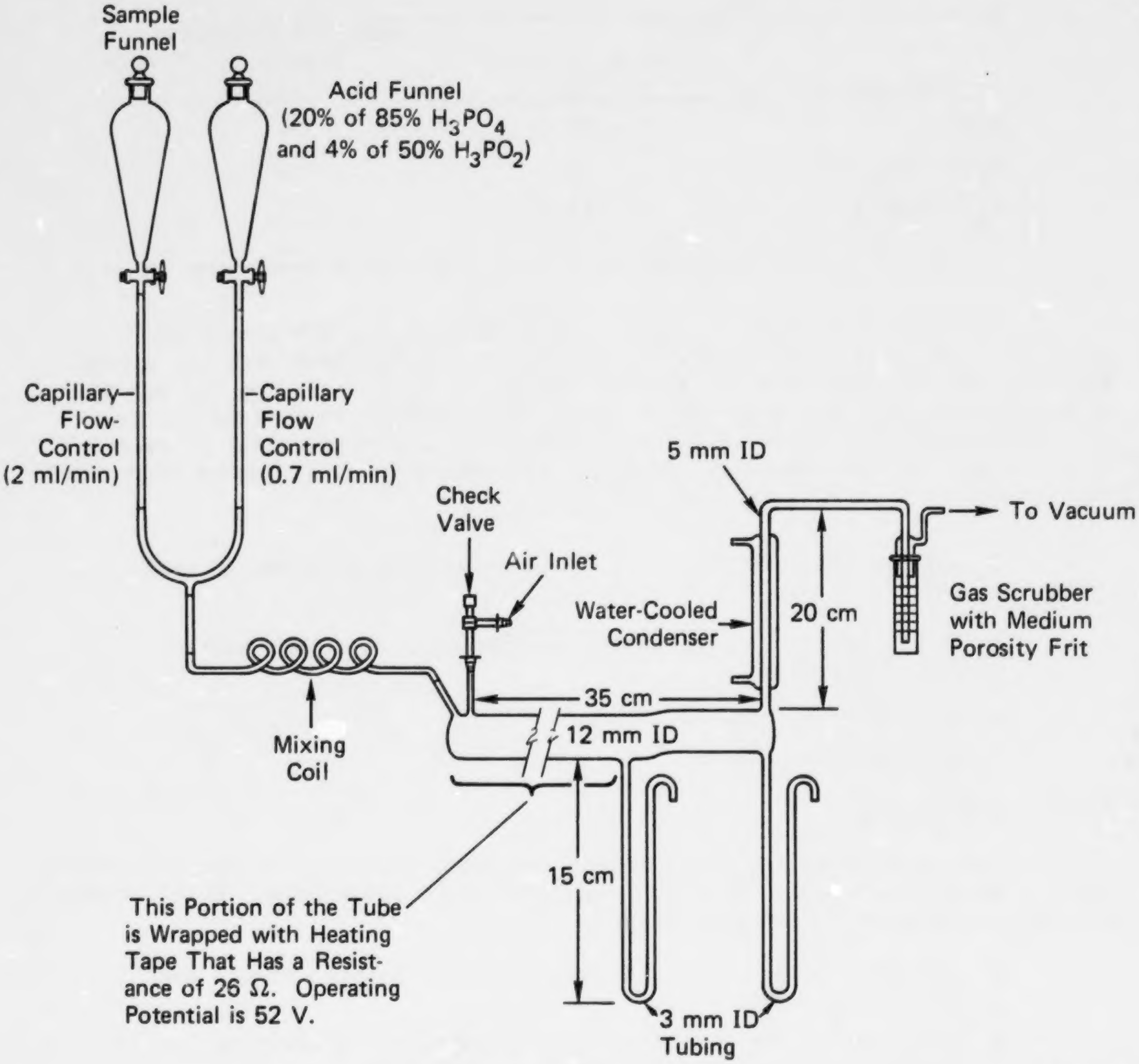
An acidified sample is allowed to flow in a thin film down a heated tube through which air is flowing. The cyanide so released is trapped in a caustic scrubber solution and manually quantitated. Presumably, because of the short residence time of the sample in the heated tube, only simple cyanides are decomposed and subsequently analyzed.

5.3.2 Procedure

The apparatus used in our investigations is depicted in Figure 5.2. The procedure is set in operation by charging the sample reservoir with water, the acid reservoir with the acid mixture described in Figure 5.2, and the absorber with 10 mL of 1.25 N NaOH diluted with enough water to give an adequate depth of liquid. The water, acid, and air were allowed to flow through the system at flow rates of 2, 0.7, and 20 mL/minute, respectively, for 5 minutes to stabilize the system. The distillation tube was heated so that approximately 60% of the sample was vaporized. The water-cooled condenser ensures that the water vapor is condensed and eliminated from the distillation tube via the waste disposal lines rather than collecting in the scrubber. The sample was transferred to the sample reservoir and allowed to pass completely through the system. The sample lines were thoroughly flushed by passing 30 mL of water through the system. The scrubber solution was transferred to a volumetric flask and brought up to volume with water, and the contents of this flask were then analyzed for cyanide using an ion-selective electrode.

5.3.3 Results and Discussion

Analyses of laboratory-prepared standards of KCN, $K_2[Ni(CN)_4]$, and $K_3[Fe(CN)_6]$ solutions were conducted with this system. The results of these investigations are shown in Table 5.2.


Sample Funnel
Acid Funnel (20% of 85% H_3PO_4 and 4% of 50% H_3PO_2)
Capillary Flow-Control (2 ml/min)
Capillary Flow Control (0.7 ml/min)
5 mm ID
To Vacuum
Check Valve
Air Inlet
Water-Cooled Condenser
20 cm
Gas Scrubber with Medium Porosity Frit
35 cm
12 mm ID
Mixing Coil
15 cm
This Portion of the Tube is Wrapped with Heating Tape That Has a Resistance of 26 Ω. Operating Potential is 52 V.
3 mm ID Tubing

SA-7854-8

Figure 5.2 Continuous-flow distillation apparatus.

TABLE 5.2 CYANIDE RECOVERIES OBTAINED WITH THE CONTINUOUS-FLOW DISTILLATION PROCEDURE

Compound	Mean recovery (%)	Relative standard deviation (%)
KCN	97.9	4
$K_2[Ni(CN)_4]$	74	6
$K_3[Fe(CN)_6]$	13.5	5

Essentially, complete recovery of cyanide from a KCN sample was possible. However, only partial recoveries of cyanide from both the nickel and iron cyanide complexes was found. To be a viable method for the analysis of simple cyanides, the procedure must be able to give complete recoveries of cyanide from the less stable cyanide complexes and essentially no recovery from the more stable cyanides. From the preceeding data, it can be seen that this procedure does not meet this criterion.

It appears that the procedure would have other problems as well. Among these are:

- Inability to analyze samples containing particulate matter due to clogging.
- Interference from sulfide
- Long analysis times.

5.3.4 Conclusions

The continuous-flow distillation procedure evaluated in our laboratory for the analysis of simple cyanides was found to be inadequate. Chief among the deficiencies of the method were:

- Inability of the method to differentiate between simple and complex cyanides.
- Inability of the method to achieve complete recovery of cyanide from complexes of moderate stability.
- Long analysis time.

With sufficient developmental work, the procedure could be modified to overcome these and other deficiencies.

5.3.5 Recommendations

In view of the performance of other methods studied, this method should be abandoned as a manual method for the analysis of simple cyanides. A significant amount of additional developmental work is necessary to produce a viable method of analysis.

5.4 EDTA ELECTRODE PROCEDURE

5.4.1 Introduction and Background

Ethylenedinitrilotetraacetic acid, also known as ethylenediaminetetraacetic acid (EDTA), is an excellent ligand for most ions. By using this reagent in a suitable environment (pH and temperature), it is possible to displace cyanide from all of the cyanide compounds studied except potassium hexacyanocobaltate(III) (see Section 4.3). Appropriate selection of the environment in which this displacement occurs should result in a system that is useful for the analysis of simple cyanides. Use of this chelate as a mask and sequestering agent have been described.[19–21] On the basis of these earlier reports, a system was developed and evaluated in the laboratory.

5.4.2 Procedure

The procedure consists of adding EDTA to an aliquot of sample made basic by the addition of 1.25 N sodium hydroxide. The sample was immersed in a water bath regulated at 40°C and stirred by means of a magnetic stirrer. After a sufficient period of time, the sample was removed from the water bath and transferred to a volumetric flask. The contents of the flask were then analyzed for cyanide using an ion-selective electrode.

5.4.3 Results and Discussion

The results of these investigations are summarized in Tables 5.3 and 5.4.

TABLE 5.3 CYANIDE RECOVERIES OBTAINED WITH THE EDTA-ELECTRODE PROCEDURE

Cyanide compound[a]	Concentration range studied (ppm CN)	Number of analyses	Mean recovery (%)	Relative standard deviation (%)
KCN				
1 , 20 min	1	9	99.9	2.7
3 , 20 min	1	6	101.1	11
3 , 45 min	1	6	100.0	3.7
10 , 60 min	1	6	101.3	8.2
CuCN				
1 , 20 min	0.5–8.8	12	71.5	29
3 , 20 min	0.7–4.2	6	86.5	8.8
3 , 45 min	1.6–7.3	12	65.5	15
10 , 60 min	1.5–7.5	5	100.1	7

(continued)

TABLE 5.3

Cyanide Compound[a]	Concentration Range Studied (ppm CN)	Number of Analyses	Mean Recovery (%)	Relative Standard Deviation (%)
$K_2[Ni(CN)_4]$				
3 mL, 20 min	0.6-2.8	6	98.3	11
3 mL, 45 min	1.4-2.8	6	88.6	6.5
10 mL, 60 min	1.1-5.4	6	110.1	5.5
$K_3[Fe(CN)_6]$				
1 mL, 20 min	1.2-1.9	5	29.3[b]	14
3 mL, 20 min	0.6-3.6	6	1.1	49
3 mL, 45 min	2.5-3.2	6	2.2	40
10 mL, 60 min	1.0-4.2	6	0.0	0
$K_3[Co(CN)_6]$				
1 mL, 20 min	0.7-2.2	6	0.0	0
3 mL, 20 min	1.2-4.3	6	0.0	0
3 mL, 45 min	0.5-5.7	6	0.0	0

[a] Each solution was prepared by adding the amount of 0.257M EDTA solution indicated and equilibrating for the time indicated.

[b] Precautions were not taken to prevent photodecomposition. When uv light is absent, the complex is stable.

TABLE 5.4 SUMMARY OF RESULTS FROM THE EDTA-ELECTRODE PROCEDURE

Cyanide compound	Mole ratio (EDTA/metal)	Mean recovery (%)	Number of samples
CuCN	< 100	68	24
	> 100	97	8
$K_2[Ni(CN)_4]$	< 600	90	8
	>1000	110	6

Both ferricyanide and cobalticyanide remain unaffected by any of the systems investigated. Recoveries of cyanide from KCN are essentially complete and also unaffected by the different experimental parameters used. Difficulties are only encountered when analyzing samples that contain CuCN or $K_2[Ni(CN)_4]$. To obtain complete recoveries of cyanide from cuprous cyanide, high EDTA:metal ratios are required. However, at these high levels a positive interference is encountered when analyzing solutions containing $K_2[Ni(CN)_4]$. Thus, there is not a clear separation between simple and complex cyanides.

To be a useful method of analysis, the method must accurately quantitate cyanide with a relatively high degree of precision. From the data included in Table 5.2, this is shown not to be the case. The relative standard deviation was found to vary from 3.7 to 29%. Another major limitation of the procedure is that it can analyze only clean samples. The cyanide is not separated from the sample matrix, which often contains a number of compounds that will interfere. In light of these disadvantages, further work using this procedure was deemed inappropriate.

5.4.4 Conclusions

The EDTA electrode procedure for analysis of simple cyanide was found to be deficient in a number of areas. Although it is a fast, simple method, complete recovery of cyanide from complexes of moderate stability was not possible and the precision was very poor. Also, the procedure is subject to a number of interferences and as a result, could be used on only the cleanest samples. Further developmental work would be necessary to overcome these difficulties.

5.4.5 Recommendations

In light of the amount of additional developmental work required by the EDTA electrode procedure and the satisfactory results obtained using other procedures, (see Sections 5.7 and 5.8), no further work along this line is recommended.

5.5 AMERICAN IRON AND STEEL INSTITUTE AERATION PROCEDURE

5.5.1 Introduction and Background

An aeration procedure for the analysis of simple cyanides described by Caruso[23] has been evaluated in our laboratory. The procedure consists of dissociating all but the most stable cyanide complexes by acidifying the sample to pH 4. The cyanide released by these complexes is aerated as hydrocyanic acid into a sodium hydroxide absorption trap. This scrubber solution is subsequently analyzed for cyanide by one of any number of analytical techniques.

5.5.2 Procedure

The apparatus used in this procedure is, but for a minor modification, the same as that used in other reflux distillation procedures.[5] This apparatus is depicted in Figure 5.3. To the absorber is added 50 mL of 1.25 N sodium hydroxide diluted with enough water to obtain a satisfactory depth of solution. The reaction flask is charged with 500 mL of sample or an aliquot of sample diluted to 500 mL. The vacuum is adjusted so that the air flow through the flask is approximately 3 liters/minute. A few drops of methyl orange indicator are added to the sample through the air inlet tube.

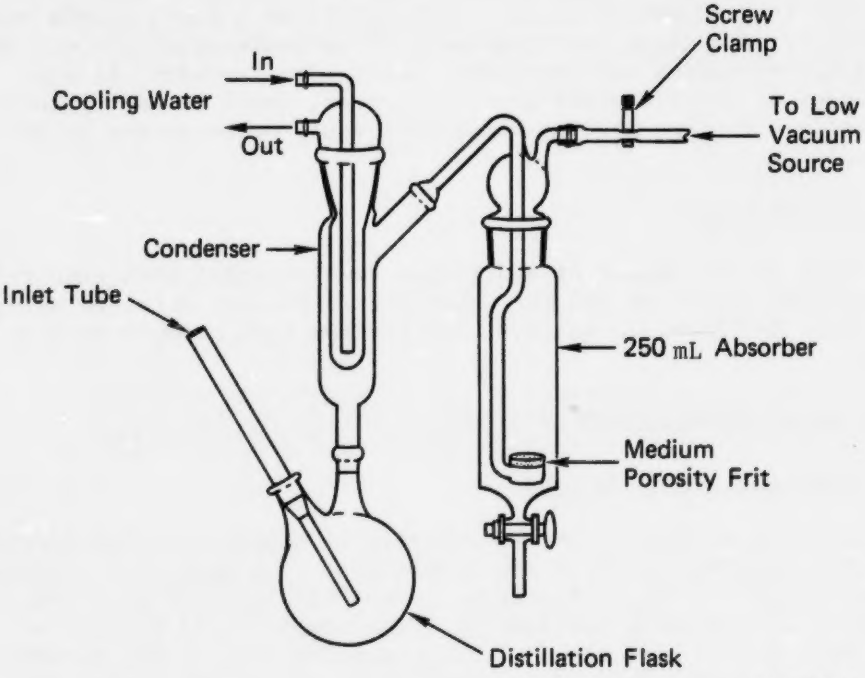

Screw Clamp
In
Cooling Water
Out
To Low Vacuum Source
Condenser
Inlet Tube
250 mL Absorber
Medium Porosity Frit
Distillation Flask
SA-7854-10

Figure 5.3 AISI aeration apparatus.

The pH of the sample is then adjusted to and maintained at 4.5 by the addition of sulfuric acid (1 + 9). Air is pulled through the sample for 2 hours, after which time the scrubber solution is quantitatively transferred to a 250-mL volumetric flask. This solution is then analyzed using an ion-selective electrode.

5.5.3 Results and Discussion

An evaluation of the AISI aeration method was conducted on prepared standards containing KCN, CuCN, $K_2[Ni(CN)_4]$, $K_3[Fe(CN)_6]$, and $K_3[Co(CN)_6]$. The recoveries, concentration range, and standard deviations found using this procedure are shown in Table 5.5. Of the cyanide compounds studied, complete recoveries of cyanide were obtained only with KCN. The reasons for the poor performance of the method with respect to recovery efficiencies from the simple cyanide species are discussed below.

TABLE 5.5 CYANIDE RECOVERIES OBTAINED WITH THE AISI AERATION PROCEDURE

Compound	Concentration range studied (ppb CN^-)	Mean recovery (%)	Relative standard Deviation (%)
KCN	1000	95.8	7.7
CuCN[a]	392-706	1.5	6
$K_2[Ni(CN)_4]$	276-534	60.2	18.9
$K_3[Fe(CN)_6]$	482-1122	0	-
$K_3[Co(CN)_6]$	558-1822	0	-

[a] The CuCN could be visually observed on the inside walls of the reaction flask above the liquid level.

The aeration of hydrocyanic acid from solution is dependent on pH, temperature, air flow rate, ionic strength, and vapor pressure. This relationship is described by the following equation.

$$(V)\ \frac{dC}{dt} = -\left(\frac{H_c C}{P}\right)(W)\left(\frac{n}{v}\right) \qquad (1)$$

$$\text{but}\quad PV = nRT$$

Rearrangement and substitution of this into equation (1) gives

$$(V)\ \frac{dC}{dt} = -\left(\frac{H_c C}{RT}\right)W$$

or

$$\frac{dC}{C} = -\left(\frac{W}{V}\right)\left(\frac{H_c C}{RT}\right)dt$$

where: V = volume of sample (L)
W = air flow rate (L minute^{-1})
H_c = Henry's law coefficient (torr mole^{-1} L)
P = atmospheric pressure
Co = initial cyanide concentrations
C = cyanide concentration at time t
R = gas law constant (62.358 $\frac{\text{torr L}}{\text{mole K}}$
T = temperature
t = time.

Solution of this differential gives:

$$\ln \frac{C}{Co} = -\left(\frac{W}{V}\right)\left(\frac{H_c}{RT}\right)t \qquad (2)$$

The ratio C/Co varies from 1 to 0. Substitution of these values into equation (2) gives the curves shown in Figures 5.4, 5.5, and 5.6, which represent aeration of cyanide under various conditions of analysis.

Based on these figures and equation (2), most of the hydrocyanic acid will have been aerated from the sample at the end of 2 hours. However, most of the compounds studied dissociate slowly at pH 4, even though the decomposition of most cyanide complexes is thermodynamically favored. As a result, the effective aeration time during an analysis is less than 2 hours and recoveries will not be complete. This is adequately depicted by the recoveries of cyanide found for the analysis of the samples containing $K_2[Ni(CN)_4]$.

Low recoveries of cyanide from cuprous cyanide are also observed when using this procedure. The compound is insoluble in water (refer to Table 4.1), and during an analysis, CuCN was observed adhering to the inside walls of the reaction flask well above the liquid level. As a result, this compound was not able to participate in the decomposition reactions.

From the above discussion, it becomes apparent that this procedure is useful only for the analysis of soluble cyanides that are kinetically labile with respect to the dissociation of cyanide. Only a relatively small number of compounds fall into this category. Since the procedure was inappropriate for the analysis all simple cyanides, further evaluation of this procedure was discontinued.

5.5.4 Conclusion

The AISI aeration method is inadequate for the analysis for simple cyanides. Although decomposition of ferricyanide is avoided, recoveries of cyanide from insoluble and/or kinetically inert complexes are incomplete. Conditions could be altered to alleviate some, if not all, of these problems, but substantial developmental work would be required (see Section 5.6).

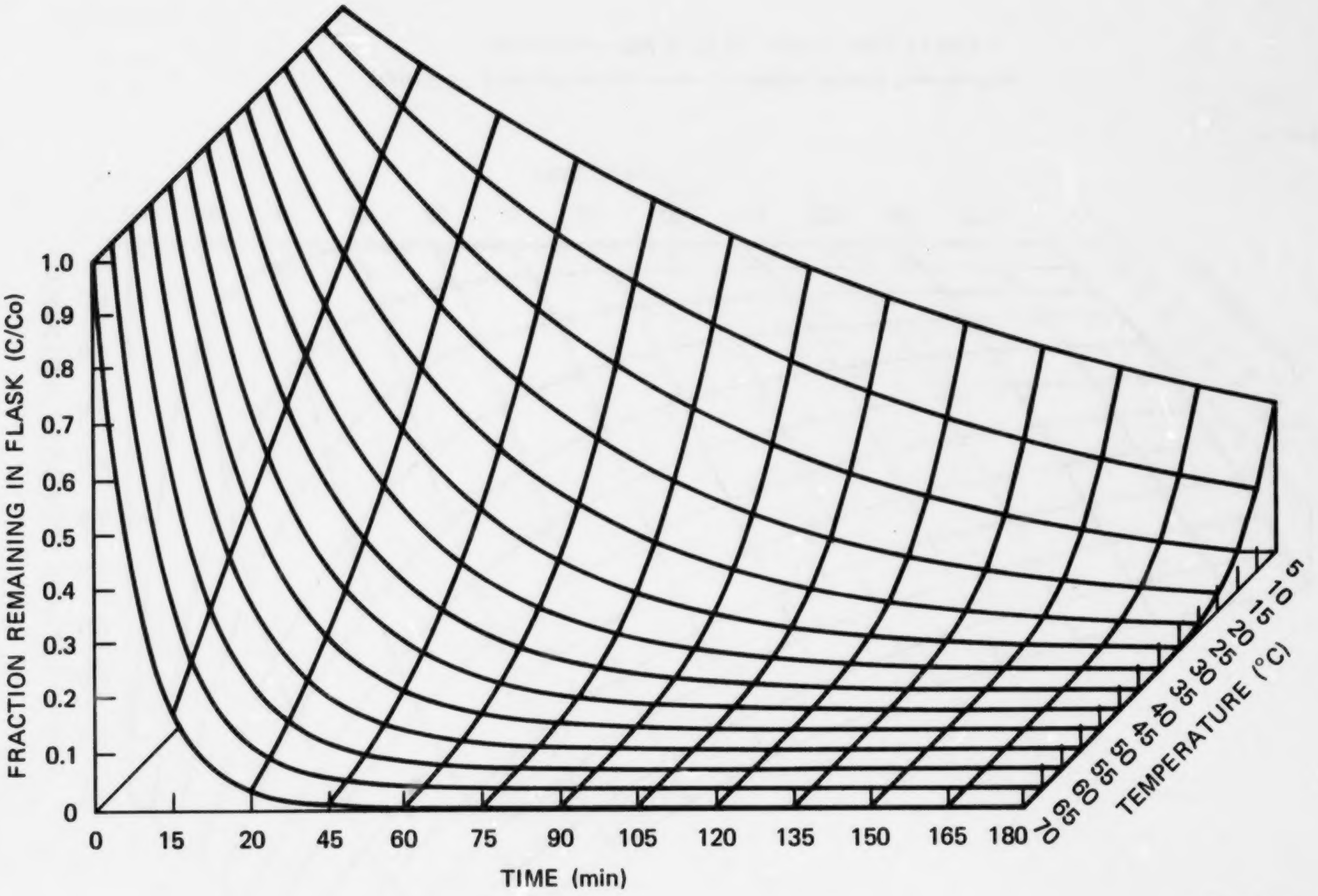


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Figure 5.4 Effect of temperature on aeration of HCN from solution.
Sample volume = 0.5 L. Air flow rate = 3 L/min.

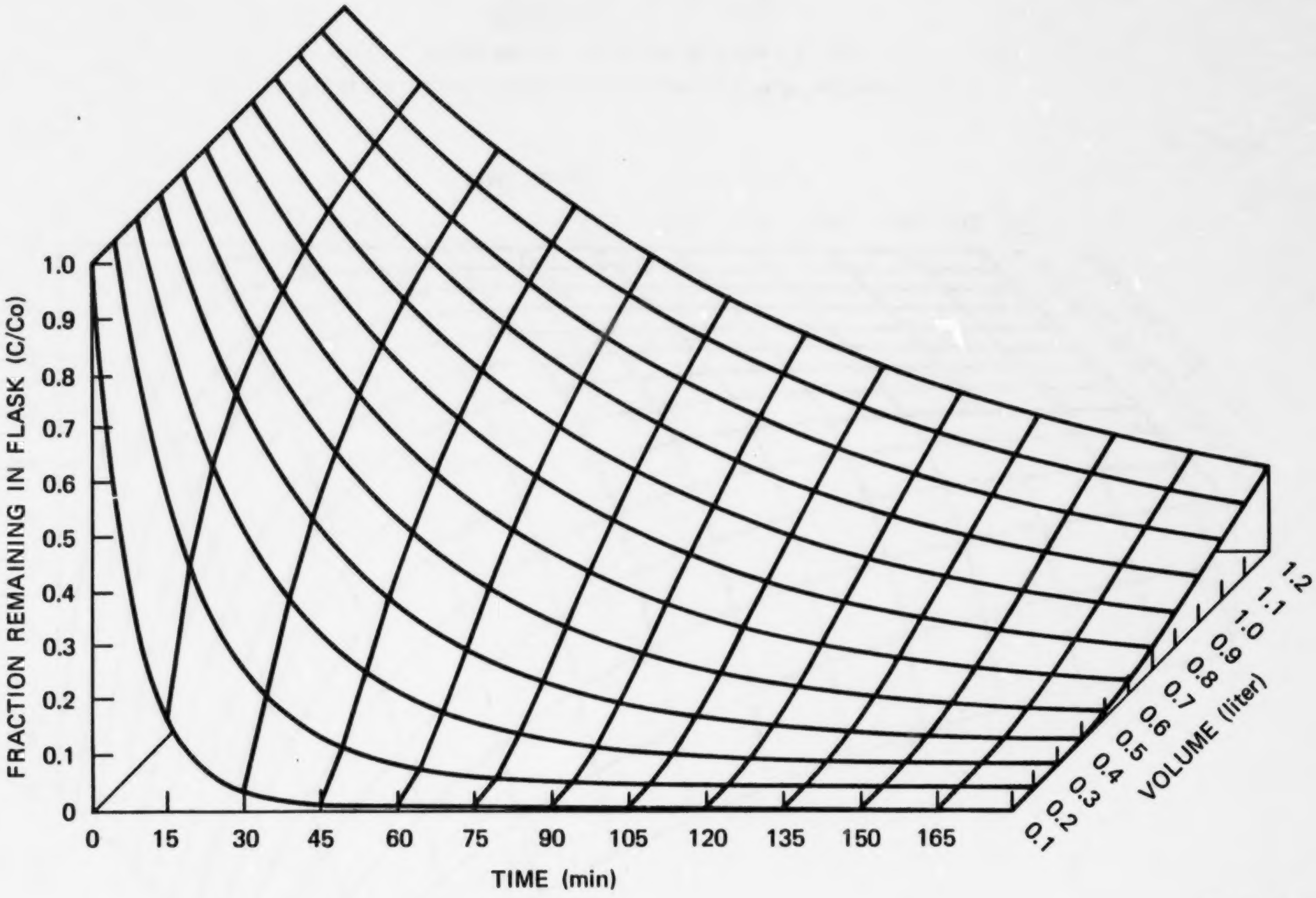

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Figure 5.5 Effect of sample volume on aeration of HCN from solution.
Temperature = 298 K (25°C). Airflow rate = 3 L/min.

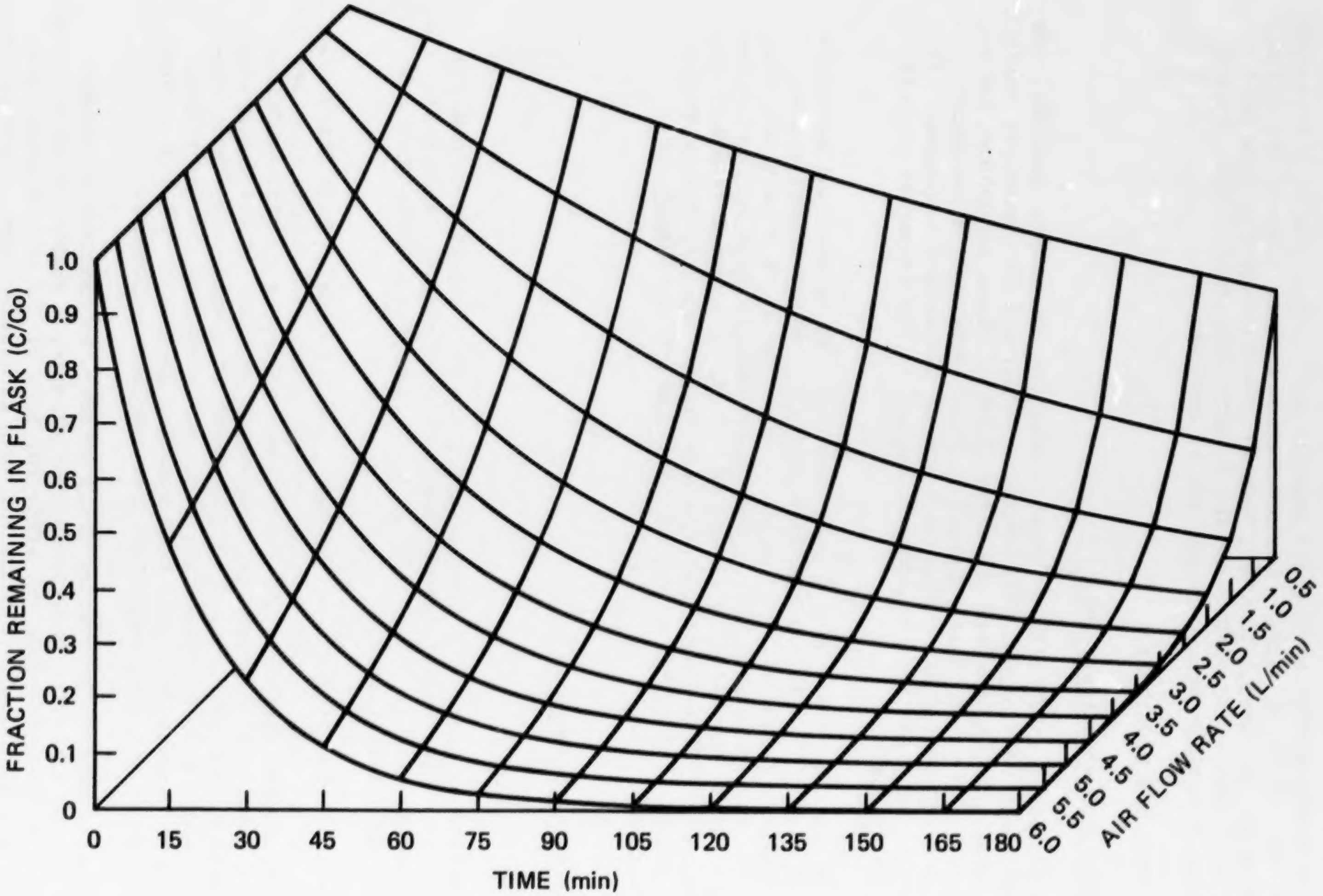

Figure 5.6 Effect of air flow rate on aeration of HCN from solution. Temperature = 298°k (25°C). Sample volume = 0.5 L.

5.5.5 Recommendations

Further developmental work would improve the performance of this method. In particular, the effect of varying key parameters such as temperature and air flow rate should be evaluated. However, because other procedures give more satisfactory performance, in particular the Roberts-Jackson distillation procedure, continued developmental work may not be desirable.

5.6 EDTA AERATION PROCEDURE

5.6.1 Introduction and Background

As stand-alone analytical methods of analysis for simple cyanides, the EDTA electrode (Section 5.4) and AISI aeration (Section 5.5) procedures exhibit serious shortcomings. To overcome the major flaws of these procedures and yet take advantage of their beneficial operating characteristics, a procedure based on a combination of these two methods was developed and evaluated. (A similar procedure has been previously described.)[24] The procedure evaluated is described in Appendix A.

Basically, the method is a 2 hour room-temperature aeration procedure carried out at a pH of 4.5 in the presence of EDTA. As previously stated, EDTA is an excellent ligand for many metals. As a result it effectively competes and displaces cyanide from the inner coordination sphere of the various metals present in the sample. The liberated cyanide is aerated from solution as hydrocyannic acid (HCN) and is subsequently trapped in a caustic scrubber solution and quantitated either titrimetrically, colorimetrically, or potentiometrically.

5.6.2 Results and Discussion

5.6.2.1 Cyanide Recoveries--

Complete recoveries of cyanide using the EDTA aeration method are found for only a limited number of the compounds studied (see Table 5.6). The remaining compounds give either partial or no recovery of cyanide when subjected to this method of analysis.

Compounds $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$, and $K_3[Co(CN)_6]$ give essentially zero recovery of cyanide. These species are not considered simple cyanides and as such should not respond. The partial recoveries of cyanide exhibited by many of the remaining compounds is, however, a problem. These incomplete recoveries arise because the rate of displacement of cyanide from these complexes by EDTA appears to be relatively slow and because of the logarithmic stripping rate of hydrocyannic acid from solution (see Section 5.5.3). Thus, the aeration time is not long enough to give complete recoveries.

These incomplete recoveries could no doubt be improved by slight modification of the analysis conditions. For example, a slight increase in temperature not only would increase the stripping rate of the hydrocyannic acid from solution, but also would increase the rate of displacement of cyanide from the complexes. This temperature change would also increase the risk of decom-

TABLE 5.6 CYANIDE RECOVERIES OBTAINED WITH THE EDTA AERATION METHOD

	Concentration of CN^-											
	2 ppm			0.2 ppm			0.02 ppm			0.006 ppm		
Compound Studied	n	Mean Recovery (%)	Relative Standard Deviation (%)	n	Mean Recovery (%)	Relative Standard Deviation (%)	n	Mean Recovery (%)	Relative Standard Deviation (%)	n	Mean Recovery (%)	Relative Standard Deviation (%)
KCN	4	98	12	4	112	8	2	98	10	4	64	16
$Cd(CN)_2$	2	100	--	2	94	--	2	102	--	2	76	--
$Co(CN)_2$	2	18	--	2	18	--	2	39	--	2	40	--
CuCN	2	81	--	2	102	--	2	66	--	2	84	--
$Fe(CN)_2$	2	98	--	2	98	--	2	87	--	2	73	--
$Fe(CN)_3$	2	91	--	2	93	--	2	67	--	2	65	--
$Hg(CN)_2$	2	35	--	2	43	--	2	43	--	2	38	--
$Mn(CN)_2$	2	95	--	2	90	--	2	98	--	2	74	--
$Ni(CN)_2$	2	82	--	2	36	--	2	54	--	2	81	--
$Zn(CN)_2$	2	92	--	2	102	--	2	103	--	2	96	--
$K_3[Cu(CN)_4]$	4	96	14	4	93	17	4	98	32	3	50	13
$K_2[Ni(CN)_4]$	2	48	--	2	57	--	2	78	--	2	40	--
$K_2[Hg(CN)_4]$	2	128	--	2	123	--	2	198	--	2	112	--
$K_3[Fe(CN)_6]$	2	0	--	2	0	--	2	0	--	2	0	--
$K_4[Fe(CN)_6]$	2	0	--	2	0	--	2	0	--	2	0	--
$K_3[Co(CN)_6]$	2	0	--	2	0	--	2	0	--	2	0	--

position of the ferri- and ferrocyanide complexes. Both these factors must be considered when devising and evaluating modifications.

Currently, the lower limit of detection is 5 ppb, higher by a factor of 2.5 than any of the other procedures evaluated. The relative standard deviation, a measure of precision of the method, is also higher. This is apparently due to the large number of experimental variables involved (see Sections 5.4 and 5.5). Suitable control of the analysis conditions should improve the precision of the method.

5.6.2.2 Interferences--

The EDTA aeration procedure is subject to a limited number of interferences, as shown by Table 5.7. The major interferences are briefly discussed below.

Chlorine--Chlorine oxidizes cyanide and thus is a negative interference. This interference can be eliminated by reduction of chlorine at the time of sample collection with ascorbic acid.

Sulfide--Sulfide will cause a positive interference to an ion specific electrode finish because of formation of hydrogen sulfide and its subsequent trapping in the caustic scrubber solution. However, the sulfide is commonly removed from the sample before storage as the lead, cadmium, or arsenic salt. Sulfide, as PbS, will not interfere as seen from the results in Table 5.7. Thus, filtration of the sample is not necessary.

Butylthiocyanate -- Because of its high volatility, this organic compound is found in the scrubber solution at the end of the analysis and interferes with the electrode finish. Because of its limited solubility in water, this substance may be removed from the sample by the extraction procedure outlined for fatty acid removal.

Co^{3+}--When added as $K_3[Co(SCN)_6]$ or $Co(SCN)_3$, this substance produces a negative interference. Apparently, cyanide exchanges with SCN^- to form the more stable, inert $Co(CN)_6{}^{3-}$ complex. This appears to be an irreversible process, although the use of another sequestering agent offers a slim chance of alleviating this problem. The SCN^- does not appear to interfere.

Hg^{2+}--When added as $K_2[Hg(SCN)_4]$, this interferes in a manner similar to that reported for Co^{3+} by forming stable mercury cyanide complexes. However, by suitable alterations in methodology this could probably be eliminated. The changes that should be investigated include higher temperatures, higher air flow rates, and different sequestering agents.

5.6.3 Conclusions

As a method of analysis for simple cyanides, the EDTA aeration method exhibits certain deficiencies. Prime among these are its partial recoveries of cyanide from some simple cyanides and its low precision. However, through suitable modification of analysis conditions, these problems could probably be eli-

TABLE 5.7 EFFECTS OF POTENTIAL INTERFERENCES ON CYANIDE RECOVERIES OBTAINED WITH EDTA AERATION PROCEDURE

Potential interference compounds	Level of interference mole:mole CN^-	Apparent Recovery of Cyanide (%) from Designated Compound				
		KCN	CuCN	$Hg(CN)_2$	$K_3[Cu(CN)_4]$	$K_4[Fe(CN)_6]$
SCN^- (as KSCN)	100:1	90	93	95	90	0
$Co(SCN)_2$	100:1	45	50	90	75	0
$K_2[Hg(SCN)_4]$	100:1	0	0	0	0	0
$K_3[Co(SCN)_6]$	100:1	53	40	105	75	0
OCN^- (as KOCN)	100:1	95	93	55	75	0
NH_4^+ (as NH_4Cl)	100:1	90	93	45	75	0
MnO_2	100:1	103	85	53	100	0
n-butylthiocyanate	100:1	1225	3250	2350	4000	2750
Butanal	100:1	38	60	43	75	0
NO_2^- (as $NaNO_2$)	100:1	90	93	48	88	0
$S^=$ (as Na_2S)	10:1	5000	4750	4500	5000	4000
	1:1	850	500	450	650	600
$S^=$ (as PbS)	100:1	100	-	-	-	-
Cl_2 (as $Ca(OCl)_2$)	10:1	0	0	0	0	0
	1:1	0	0	0	0	0

Note: Concentration of cyanide was 0.2 ppm in all test solutions.

minated. The procedure is unaffected by the presence of thiocyanate and sulfide, as lead sulfide. The other interferences can be eliminated from the sample before analysis.

5.6.4 Recommendations

Through suitable modification, the performance of this procedure with respect to cyanide recoveries could be substantially improved. Studies of these modifications should be conducted, especially in light of its satisfactory performance in the presence of thiocyanate and lead sulfide. These new lines of investigation should include a study of the effect of temperature, air flow rate, analysis time, and different sequestering agents. After optimization of conditions, the procedure should be evaluated on a number of compounds in the presence and absence of suspected interferences.

5.7 EPA PROCEDURE FOR CYANIDES AMENABLE TO CHLORINATION

5.7.1 Introduction and Background

A procedure for the analysis of simple cyanides, or more appropriately "cyanides amenable to chlorination" (CATC), that has attained widespread use and is currently recommended by the Environmental Protection Agency was evaluated. This procedure is based on the difference between two analyses for total cyanide. An unadulterated aliquot of the sample and an aliquot of the sample that has been chlorinated (thereby destroying the CATC) are subjected to the total cyanide distillation procedure. The difference in the cyanide content of these two samples is defined to be the CATC. The cyanide in the absorption solution is determined by any one of a number of different analytical techniques.

This procedure relies on the total cyanide methodology presented in Section 4.4. All the information contained in that section is equally applicable here. The method is described in detail in Appendix E.

5.7.2 Results and Discussion

5.7.2.1 Cyanide Recoveries--

The results of the evaluation of the CATC procedure are shown in Table 5.8. Each cyanide compound falls into one of three categories: those that are not chlorinated at all; those that are partially chlorinated; and those that are completely chlorinated. This latter category is restricted to those species that are easily dissociable in water and of only moderate stability. Inlcuded in this group are: KCN, $Cd(CN)_2$, $Cu(CN)$, $Fe(CN)_2$, $Fe(CN)_3$, $Mn(CN)_2$, $Zn(CN)_2$, and $K_3[Cu(CN)_4]$. The compounds that are not at all chlorinated are $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$, $K_3[Co(CN)_6]$, and nitriles. These complexes are very stable and/or kinetically inert, whereas the nitriles are easily hydrolyzed to the corresponding acid and ammonia under the conditions of analysis.

The remaining compounds--$Ni(CN)_2$, $Hg(CN)_2$, $K_2[Ni(CN)_4]$, and $K_2[Hg(CN)_4]$--are only partially chlorinated and so fall into the second category. The degree of chlorination of these compounds depends on the initial concentration of the compound. Presumably only dissociated CN^- groups are chlorinated,

TABLE 5.8 CYANIDE RECOVERIES OBTAINED WITH EPA METHOD "CYANIDES AMENABLE TO CHLORINATION" USING AN ION-SELECTIVE ELECTRODE

	Concentration of CN^-											
	0.002 ppm			0.02 ppm			0.2 ppm			2 ppm		
Compound Studied	n	Mean Recovery (%)	Relative Standard Deviation (%)	n	Mean Recovery (%)	Relative Standard Deviation (%)	n	Mean Recovery (%)	Relative Standard Deviation (%)	n	Mean Recovery (%)	Relative Standard Deviation (%)
Simple Cyanides												
KCN	6	87	8	6	99	2	6	100	0.5	6	100	0.5
$Cd(CN)_2$	4	48	20	4	101	14	4	102	2	4	99	4
$Co(CN)_2$	4	127	24	4	45	3	4	3.5	8	4	-1	3
CuCN	1	92	-	1	99	-	1	94	-	1	98	-
$Fe(CN)_2$	1	96	-	1	100	-	1	100	-	1	108	-
$Fe(CN)_3$	1	46	-	1	83	-	1	90	-	1	99	-
$Hg(CN)_2$	4	48	93	4	93	42	4	89	6	4	59	5
$Mn(CN)_2$	1	50	-	1	93	-	1	97	-	1	96	-
$Ni(CN)_2$	4	101	19	4	76	2	4	64	4	4	33	2
$Zn(CN)_2$	1	76	-	1	99	-	1	99	-	1	104	-
Complex Cyanides												
$K_3[Cu(CN)_4]$	6	130	104	6	96	7.8	6	97	3.4	6	101	4
$K_4[Fe(CN)_6]$	6	-41	9	6	-5	5	6	0	4	6	-0.4	3
$K_3[Fe(CN)_6]$	6	-30	6	6	-2	6	6	0.3	3	6	1	3
$K_2[Hg(CN)_4]$	4	30	157	4	99	0.6	4	92	2	4	81	3
$K_2[Ni(CN)_4]$	6	70	11	4	59	5	4	48	3	4	30	2
$K_3[Co(CN)_6]$	6	0	-	6	2.5	14	6	-0.1	12	6	0.1	5
Organic Cyanides												
CH_3CN	6	0	-	6	0	-	6	0	-	6	0	-
$CH_3CH_2CH_2CN$	1	0	-	1	0	-	1	0	-	1	0	-

so that metal-bound groups are protected. The degree of dissociation is concentration dependent. At lower concentrations, a higher percentage of cyanide will be dissociated, which results in chlorination of a larger fraction of the total sample. Figure 5.7 shows the recoveries of cyanide from several complexes as a function of their initial concentration.

The mechanism of chlorination generally proceeds along the following lines. The cyanide present in the sample is oxidized to cyanogen chloride (CNCl), which is then hydrolyzed to cyanate (CNO^-). The hydrolysis of cyanogen chloride is both pH and time dependent. At pH 9, with no excess chlorine present, cyanogen chloride may persist for 24 hours. The cyanate produced by CNCl hydrolysis can be further oxidized with chlorine at near neutral pH to carbon dioxide and nitrogen. Upon acidification, cyanate will be converted to ammonia.

Although the method exhibits a number of deficiencies, there are two areas that should be explored further in an effort to improve the method. These are briefly discussed below.

The oxidizing ability of the hypohalous acid used is directly dependent on pH. The dissociation constant of HOCl, 3.4×10^{-8}, and the standard oxidation-reduction potentials for reactions of the halogens (tabulated below) indicate that chlorination of cyanide would proceed more readily at a lower pH than that currently being used.

TABLE 5.9 STANDARD REDUCTION POTENTIALS OF CHLORINATING SPECIES

$H^+ + HOCl + e^- \rightleftharpoons 1/2\ Cl_2 + H_2O$	1.63
$1/2\ Cl_2 + e^- \rightleftharpoons Cl^-$	1.36
$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	0.89

If the rate-limiting step of the chlorination reaction is the dissociation of the cyanide complexes, the use of stronger oxidizing agents may have no effect on the chlorination. If, however, direct oxidation of the metal cyanide compounds becomes a major contributing pathway for the chlorination reaction as a result of the increased oxidation potentials, then the use of different pH values should prove beneficial. A laboratory investigation to determine the pH dependence and/or mechanism of this reaction should be conducted to develop a more efficient chlorination procedure.

Another avenue of investigation is based on a short-cut method for the analysis of simple cyanides.[33] This procedure involves the chlorination of free cyanide or cyanide that has been displaced from various metal-cyanide compounds by EDTA. It may be possible to adapt this type of chlorination procedure for use here.

Either one or both of these approaches should be investigated in an attempt to alleviate the deficiencies of this procedure with respect to recoveries.

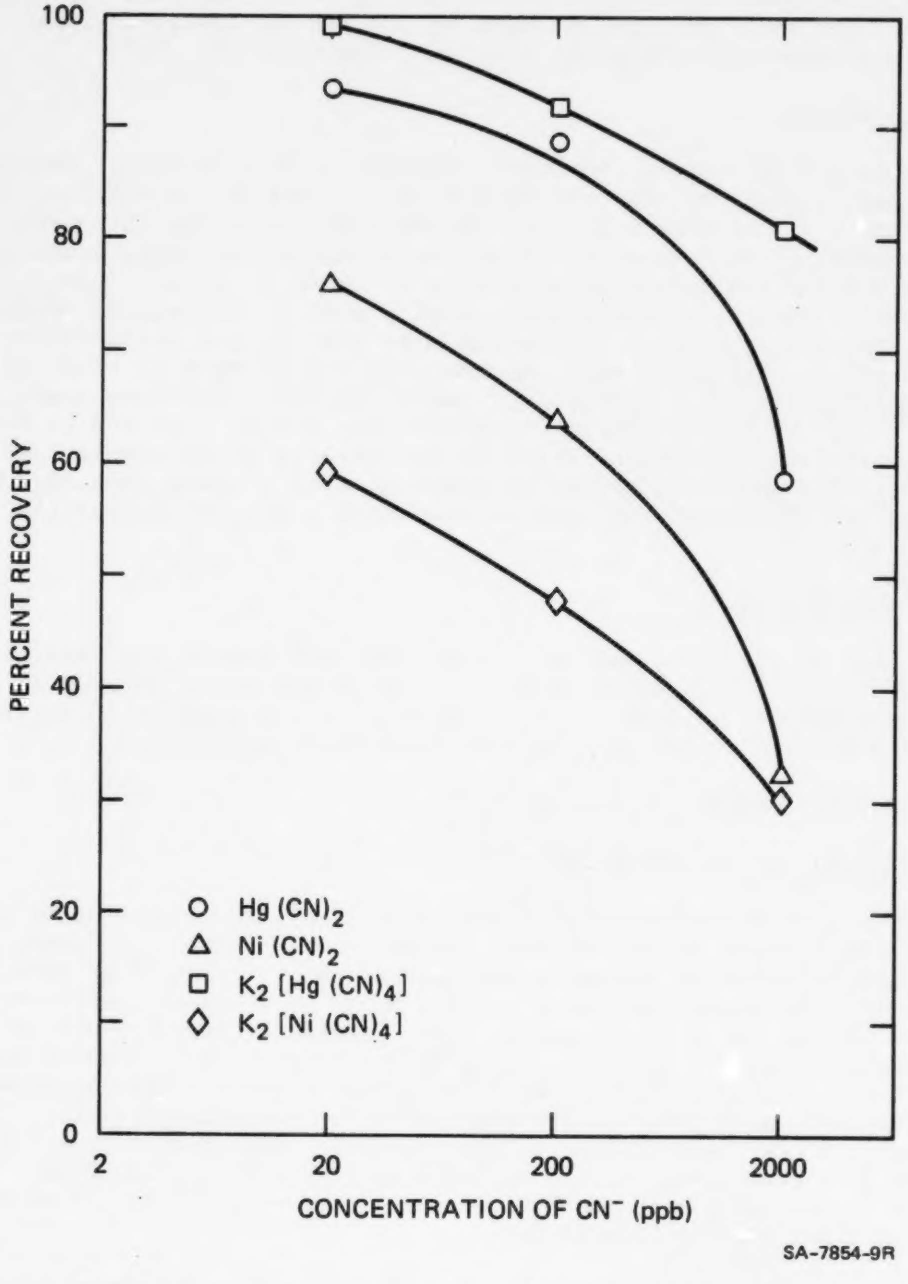

Figure 5.7 Recovery of cyanide from mercury and nickel cyanide compounds as a function of initial cyanide concentration, using EPA CATC procedure.

5.7.2.2 Interferences--

This method, as previously stated, uses the EPA method for total cyanides (see Section 4.4). Therefore, it is subject to the same interferences as the method for total cyanide, as shown by the results listed in Table 5.10. A discussion of these interferences in given in Section 4.4.

5.7.3 Conclusions

The method of analysis "Cyanides Amenable to Chlorination," was originally designed to indicate the treatability of cyanides by the alkaline chlorination process. It has become apparent during this study that this method exhibits a number of deficiencies. There are primarily two major areas of concern; these are (A) the method is subject to a number of interferences, and (b) the method is unable to definitely classify some of the cyanide compounds studied as either treatable or not treatable by the alkaline chlorination process. This latter problem is most apparent when one attempts to classify the compounds $Hg(CN)_2$, $Ni(CN)_2$, $K_2[Hg(CN)_4]$, and $K_2[Ni(CN)_4]$; in these cases, the percentage of the compound chlorinated varies over a wide range and is directly dependent on the initial concentration of the compound in the sample (see Figure 5.7). It should be possible to alleviate some of these problems through a more judicious choice of chlorination conditions and/or digestion-distillation procedures.

5.7.4 Recommendations

Because of the widespread use of the EPA CATC method, its deficiencies should be corrected. A different total cyanide method should be used to overcome the interference problems (see Section 4.3). An evaluation to determine the most efficient chlorination conditions is also recommended.

5.8 MODIFIED ROBERTS-JACKSON PROCEDURE

5.8.1 Introduction and Background

The procedure investigated in this study was a slight variation of the Wood-River modification of the procedure developed by Roberts and Jackson,[25] which has been reported to measure cyanides equivalent to "cyanides amenable to chlorination." The method evaluated in this study is based on converting to hydrocyanic acid all but the most refractory metal-cyanide complexes from a slightly acidified sample during a one-hour reflux distillation. The liberated gas (HCN) is absorbed in a sodium hydroxide solution, which is subsequently analyzed for cyanide either volumetrically, colorimetrically, or potentiometrically. The procedure avoids the dissociation of iron cyanides, compounds not considered to be amenable to chlorination, by the addition of zinc and lead acetates. The Zn^{2+} and Pb^{2+} presumably form insoluble double salts with the iron cyanides, thereby preventing their decomposition.

Inclusion of such "fixing agents" in distillation procedures to prevent the decomposition of the iron cyanides is not a new idea. The use of lead nitrates,[26] lead acetate,[27] and zinc acetate[28] have been reported in earlier publications. For various reasons, the procedure developed by Roberts and Jackson and later modified at Wood River has gained the widest acceptance, and it was

TABLE 5.10 EFFECTS OF POTENTIAL INTERFERENCES ON CYANIDE RECOVERIES OBTAINED WITH THE EPA PROCEDURE "CYANIDES AMENABLE TO CHLORINATION" USING AN ION-SELECTIVE ELECTRODE FINISH

Potential interference compounds	Level of interference mole:mole of CN^-	Apparent recovery of cyanide (%) from designated compound				
		KCN	CuCN	$Hg(CN)_2$	$K_3[Cu(CN)_4]$	$K_4[Fe(CN)_6]$
KSCN	100:1	19000	19000	16000	28000	35000
	1:1	159	119	200	120	120
$Co(SCN)_2$	100:1	31400	18800	27700	24300	39500
	1:1	128	66	246	118	300
$K_2[Hg(SCN)_4]$	100:1	17800	-	22500	-	-
	1:1	301	-	342	-	-
$K_3[Co(SCN)_6]$	100:1	99000	-	93200	-	-
	1:1	320	-	695	-	-
n-butylthiocyanate	100:1	5	-	700	-	-
	1:1	50	-	70	-	-
OCN^- (as KOCN)	100:1	100	99	83	103	-5
	1:1	-	-	84	-	-
NH_4^+ (as NH_4Cl)	100:1	57	96	45	106	-5
	1:1	100	94	80	-	-
NO_2^- (as $NaNO_2$)	100:1	66	81	58	103	1
	1:1	100	99	84	-	-
MnO_2	100:1	99	99	81	109	-5
	1:1	-	-	-	-	-
Butanal	100:1	55	97	93	88	5
	1:1	92	-	-	105	-
$S^=$ (as Na_2S)	10:1	2800	4680	3370	3770	3420
	1:1	250	240	190	185	75
Cl_2 (as $Ca(OCl)_2$)	10:1	0	-0.5	-11	-0.5	-100
	1:1	0	0	-17	-0.4	-98.6

Note: Cyanide concentration level was 0.2 ppm in all test solutions.

a slight variation of this Wood River procedure that was investigated in our laboratory. The modification, which was made at the request of the Project Officer, consisted of substituting lead acetate for one-half of the zinc acetate. The procedure used is described in Appendix B.

5.8.2 Results and Discussion

5.8.2.1 Cyanide Recoveries--

The cyanide recoveries from this method are shown in Table 5.11. A useful method for the analysis of "simple" cyanides must meet two criteria. First, the method must show complete recovery from all the metal cyanides equivalent to "cyanides amenable to chlorination." In addition, little or no recovery should be observed from the most refractory metal cyanides, which inincludes $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$, and $K_3[Co(CN)_6]$. This method comes close to fulfilling these requirements. The main deficiency is the incomplete recovery of cyanide from the mercuric compounds. This is not a surprising result, since the mercury compounds are quite stable (β_4 for $Hg(CN)_4^{2-}$ is 10^{41}). The recoveries are inversely dependent on the concentration of the metal complex. The higher recoveries observed at lower concentration are presumably due to the greater degrees of dissociation of the metal complex, which is expected in more dilute solutions.

It should be possible, by lowering the pH, to improve recoveries of CN^- from the mercury compounds without adversely affecting the response to the iron cyanides. However, in a brief study, the same recoveries were obtained at pH values of 3.8 and 2.5.

On the basis of the performance of the ligand-exchange procedure for total cyanide, it was felt that improved recoveries of cyanide from the mercury compounds would be possible if a selective sequestering agent was added. An abbreviated study was conducted to evaluate this and it was found that in the presence of chloride ion, as sodium chloride, the recoveries of cyanide from $Hg(CN)_2$ at 2 ppm CN increased from 22% to approximately 80%. These improved recoveries are due to the displacement of cyanide by chloride to form the insoluble $HgCl_2$.

5.8.2.2 Interferences--

A number of experiments were conducted to determine the effect of various compounds on the performance of the modified Roberts-Jackson method. As shown in Table 5.12, the procedure is subject to only a relatively small number of interferences, which are breifly discussed below.

MnO_2--At high levels, MnO_2 appears to cause a slight positive interference, as observed during our analysis of samples of ferrocyanide. However, the magnitude of this interference may be statistically insignificant.

Chlorine--Under the conditions of analysis, chlorine oxidizes all cyanide species and thus produces very low recoveries. Since recovery of cyanide from ferrocyanide is already low, the presence of chlorine does not have any adverse effect on this sample. Procedures for removing chlorine from the sample before analysis are described in Appendix B.

TABLE 5.11 CYANIDE RECOVERIES OBTAINED WITH THE MODIFIED ROBERTS-JACKSON PROCEDURE

Compound Studied	Concentration of CN^-											
	0.002 ppm			0.02 ppm			0.2 ppm			2 ppm		
	n	Mean Recovery (%)	Relative Standard Deviation (%)	n	Mean Recovery (%)	Relative Standard Deviation (%)	n	Mean Recovery (%)	Relative Standard Deviation (%)	n	Mean Recovery (%)	Relative Standard Deviation (%)
KCN	4	115	13	4	104	9	4	100	0	4	100	0
$Cd(CN)_2$	2	120	--	2	110	--	2	100	--	2	100	--
$Co(CN)_2$	2	120	--	2	51	--	2	7	--	2	9,34	--
CuCN	2	115	--	2	102	--	2	99	--	2	96	--
$Fe(CN)_2$	2	120	--	2	100	--	2	100	--	2	96	--
$Fe(CN)_3$	2	125	--	2	100	--	2	100	--	2	100	--
$Hg(CN)_2$	2	140	--	2	100	--	2	82	--	2	22	--
$Mn(CN)_2$	2	135	--	2	100	--	2	100	--	2	100	--
$Ni(CN)_2$	2	120	--	2	100	--	2	100	--	2	100	--
$Zn(CN)_2$	2	125	--	2	100	--	2	100	--	2	100	--
$K_3[Cu(CN)_4]$	2	155	--	4	101	2	4	99	2	4	100	0
$K_2[Ni(CN)_4]$	2	135	--	2	100	--	2	100	--	2	100	--
$K_2[Hg(CN)_4]$	2	153	--	2	100	--	2	74	--	2	75	--
$K_3[Fe(CN)_6]$	2	0	--	2	7	--	2	2	--	2	1	--
$K_4[Fe(CN)_6]$	2	0	--	2	6	--	2	1	--	2	1	--
$K_3[CO(CN)_6]$	2	0	--	2	0	--	2	0	--	2	0	--

TABLE 5.12 EFFECTS OF POTENTIAL INTERFERENCES ON CYANIDE RECOVERIES WITH THE MODIFIED ROBERTS-JACKSON PROCEDURE

		Apparent recovery of cyanide (%) from designated compound				
Potential interference	Level mole:mole CN	KCS	CuCN	$Hg(CN)_2$	$K_3[Cu(CN)_4]$	$K_4[Fe(CN)_6]$
SCN^- (as KSCN)	100:1	100	98	84	100	0
NO_2^- (as $NaNO_2$)	100:1	100	100	82	108	0
NH_4^+ (as NH_4Cl)	100:1	100	100	68	100	0
OCN^- (as KOCN)	100:1	100	100	56	100	0
MnO_2	100:1	96	82	68	100	0
$Co(SCN)_2$	100:1	72	60	68	88	0
	10:1	100	70		60	
$K_2[Hg(SCN)_4]$	100:1	0	0	0	0	0
$K_3[Co(SCN)_6]$	100:1	62	58	100	95	0
Butanal	100:1	100	94	75	100	0
Cl_2 (as $Ca(OCl)_2$)	10:1	0	0	0	0	0
	1:1	0	0	0	0	0
$S^=$ (as Na_2S)	10:1	100	100	100	92	0
	1:1	100	90	100	100	0
n-butylthiocyanate	100:1	4500	7400	9000	10000	10000
	10:1	1500	1700	1900	1400	1100

Note: Cyanide concentration was 0.2 ppm in all test solutions.

Sulfide--Sulfide does not interfere with any of the analyses except for samples containing mercury complexes. The sulfide is precipitated out of the sample as the insoluble PbS. This precipitate is stable under the conditions of analysis and hence does not interfere. The positive interference observed during analysis of the $Hg(CN)_2$ sample is somewhat misleading. Recoveries of only 82% have been found on samples containing only $Hg(CN)_2$. In the presence of sulfide, there is 100% recovery of CN. Apparently, the cyanide is displaced from mercury by the formation of HgS. Any additional sulfide remaining after this reaction is then removed from solution by precipitation as lead sulfide. It should be stressed that no sulfide is found in the scrubber.

The absence of sulfide interference is significant. Sulfide should still be removed from solution when the sample is collected by precipitation as lead sulfide to prevent oxidation and autocatalytic reaction with cyanide to form thiocyanate. However, filtration to remove this precipitate is not necessary. This avoids the loss of insoluble cyanides during the filtration step.

$K_2[Hg(SCN)_4]$--This produces a substantial negative interference on the analysis. Apparently, the tetracyanomercurate, or a mixed ligand system consisting of cyanide and thiocyanate is formed. The reason for these incomplete recoveries from mercury compounds has previously been discussed.

$Co(SCN)_2$ and $K_3[Co(SCN)_6]$--These two compounds both exhibit a negative interference for the same reason as $K_2[Hg(SCN)_4]$. A cobalt-cyanide complex forms that, because of its high stability, will not release cyanide during the distillation.

Butylthiocyanate--During the distillation, butylthiocyanate is distilled over into the scrubber solution and interferes with the electrode finish. Because of its limited solubility in water, this compound can probably be removed by the extraction procedure described for the removal of fatty acids.

5.8.3 Conclusions

The modified Roberts-Jackson procedure for the analysis of simple cyanides is far superior to any other method investigated. The procedure provides a clear distinction between the different types of cyanides in solution and is relatively free of interferences. For those compounds that do interfere, other pretreatment methods have been described that will alleviate the problem. Most significantly, the interferences from sulfide and thiocyanate have been completely eliminated. A deficiency of the procedure is the incomplete recovery of cyanide from $Hg(CN)_2$ and $K_2Hg(CN)_4$ from samples with greater than 20 ppb CN^-.

5.8.4 Recommendations

On the basis of its performance in this study, the modified Roberts-Jackson method comes nearest to being a universal method for cyanides equivalent to "cyanides amenable to chlorination." Its only serious deficiency is the incomplete recovery of cyanide from the mercury complexes. This could probably be overcome by the addition of a highly selective sequestering agent, such as

TEP. Because of the low affinity of this ligand for ferric and ferrous ions, its addition would probably not affect cyanide recoveries from the iron cyanide complexes. Further work should be supported to evaluate such a modification.

5.9 COMPARISON OF SIMPLE CYANIDE METHODS

Qualitative comparisons of the performance of those methods studied in depth with respect to recoveries, interferences, and statistical parameters are depicted in Tables 5.13, 5.14, and 5.15, respectively.

The best method of analysis for simple cyanides appears to be the modified Roberts-Jackson method. The procedure not only gives complete recovery of cyanide from most of the simple cyanides, but also is unaffected by the presence of sulfide and thiocyanate. The other interferences can be removed before distillation. Some additional development work is warranted on the basis of these results, but not to the degree required by the other methods.

As previously discussed, the procedure for cyanides amenable to chlorination and the EDTA-aeration procedure could be improved by further developmental work. The major concern is improvement of cyanide recoveries from the simple cyanides. Significant benefits could be obtained from some developmental work in this area. However, the major limitationn of the CATC procedure is its inability to accurately assess cyanide levels in the presence of either sulfide or thiocyanate. It appears that these interferences can be eliminated only with extensive developmental work.

TABLE 5.13 COMPARISON OF CYANIDE RECOVERIES FROM THE SIMPLE CYANIDE METHODS

	Concentration Level								
	2000 ppb CN^-			200 ppb CN^-			20 ppb CN^-		
Compound Studied	A	B	C	A	B	C	A	B	C
KCN	C	C	C	C	C	C	C	C	C
$Cd(CN)_2$	C	C	C	C	C	C	C	C	C
$Co(CN)_2$	N	S	S	S	S	S	S	S	M
CuCN	C	M	C	C	C	C	C	M	C
$Fe(CN)_2$	C	C	C	C	C	C	C	M	C
$Fe(CN)_3$	C	C	C	C	C	C	M	M	C
$Hg(CN)_2$	M	S	S	M	S	M	C	S	C
$Mn(CN)_2$	C	C	C	C	C	C	C	C	C
$Ni(CN)_2$	S	M	C	M	S	C	M	M	C
$Zn(CN)_2$	C	C	C	C	C	C	C	C	C
$K_3[Cu(CN)_4]$	C	C	C	C	C	C	C	C	C
$K_2[Ni(CN)_4]$	S	S	C	M	M	C	M	M	C
$K_2[Hg(CN)_4]$	M	C	M	M	C	M	C	C	C
$K_3[Fe(CN)_6]$	N	N	N	N	N	N	N	N	N
$K_4[Fe(CN)_6]$	N	N	N	N	N	N	N	N	N
$K_3[Co(CN)_6]$	N	N	N	N	N	N	N	N	N

A = EPA--Cyanides Amenable to Chlorination
B = EDTA-Aeration
C = Modified Roberts-Jackson

N = None (<10%)
S = Slight (11%-50%)
M = Moderate (51%-90%)
C = Complete (>90%)

TABLE 5.14 COMPARISON OF INTERFERENCE EFFECTS ON THE SIMPLE CYANIDE METHODS

Compound studied for interference	Level mole:mole CN^-	EPA	EDTA-aeration	Modified Roberts-Jackson
SCN^-	100:1	++	0	0
	10:1	++	0	0
NO_2^-	100:1	0	0	0
NH_4^+	100:1	0	0	0
OCN^-	100:1	0	0	0
MnO_2	100:1	0	0	0
$Co(SCN)_2$	100:1	++	-	-
	10:1	++		-
$K_2[Hg(SCN)_4]$	100:1	++	--	--
	10:1	++	--	--
$K_3[Co(SCN)_6]$	100:1	++	-	-
	10:1	++		-
Butanal	100:1	-	-	-
	10:1	-		
Cl_2 (as $Ca(OCl)_2$)	10:1	--	--	--
	1:1	--	--	--
$S^=$ (as Na_2S)	10:1	++	++[a]	0
	1:1	++	++[a]	0
Butylthiocyanate	100:1	++	++	++
	10:1	++	++	++

[a] If present as PbS, there will be no interference.

++ = Severe positive interference.
+ = Slight to moderate positive interference.
0 = No interference.
- = Slight to moderate negative interference
-- = Severe negative interference.

TABLE 5.15 COMPARISON OF VARIOUS OPERATING PARAMETERS FOR THE SIMPLE CYANIDE METHODS

	EPA	EDTA-aeration	Modified Roberts-Jackson
Lower limit of detection (ppb)	2	5	2
Relative standard deviation above 20 ppb CN^-	~8%	~10%	~4%
Length of analysis (minimum)	1.5 hr	2.5 hr	1.5 hr

SECTION 6

THIOCYANATE METHODOLOGY

6.1 INTRODUCTION

In the early 1960s, Ayres and Baird[29] reported an analytical method for cupric ion that was based on the extraction of a brightly colored, neutral dithiocyanatodipyridylcopper(II) complex.* Later Danchik and Boltz[31] adapted this procedure to use for thiocyanate analysis, and included quantitation of low levels of flame atomic absorption spectroscopy of the copper. The colorimetric procedure for thiocyanate was reinvestigated in addition, evaluations were made of two new variations of this method that involve either high performance liquid chromatography or graphite furnace atomic absorption spectroscopy.

6.2 COLORIMETRIC METHODS OF ANALYSIS

In the presence of excess pyridine, the $Cu(Py)_2(SCN^-)_2$ complex is readily extracted into chloroform, with a distribution ratio reported by Ayres and Baird[30] of 10^4. Figure 6.1 shows the visible absorption spectra of the chloroform extract at various thiocyanate concentrations. The spectrum is characterized by a λ_{max} at 407 nm with an extinction coefficient of 810 L $mole^{-1}cm^{-1}$. Conformity to Beer's law was observed between 2-40 ppm SCN^-. The chloroform extract is stable for more than 24 hours if properly stored.

Quantitation based on this visible absorption is limited by the small extinction coefficient of the complex. Assuming an original aqueous sample volume of 20 mL , the lower limit of detection is 0.2 ppm SCN^- in the aqueous sample.

An attempt was made to lower the detection limit by modifying the colorimetric procedure. The pyridine ligands do not directly contribute to the visible absorption spectrum of the complex, but they do exhibit a complex set of aromatic $\Pi \rightarrow \Pi^*$ UV bands between 230-270 nm, as shown in Figure 6.2. To make use of the absorption bands for the analysis of thiocyanate, it is necessary to use a solvent that has a cutoff wavelength sufficiently below the λ_{max} of these absorption bands. (The cutoff wavelength of chloroform is 250 nm.) In the spectrum of the copper complex in methanol, the $\Pi \rightarrow \Pi^*$ UV bands of pyridine are slightly broadened and are superimposed on the tail of an intense band at higher

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[*] The copper is not extracted into $CHCl_3$ in the absence of excess pyridine. Therefore, it may be that the species that is actually extracted is $Cu(SCN^-)_2Py_4$ species.

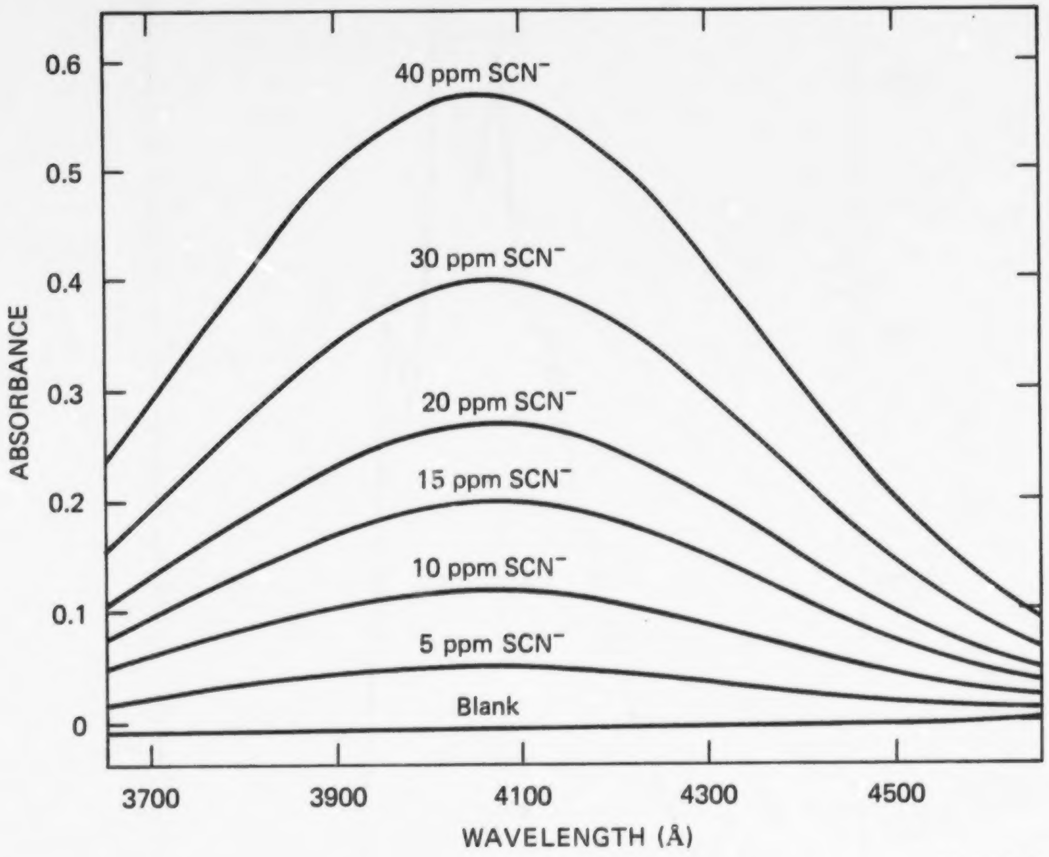

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Figure 6.1 Absorption spectra of dithiocyanatodipyridylcopper(II) in chloroform.

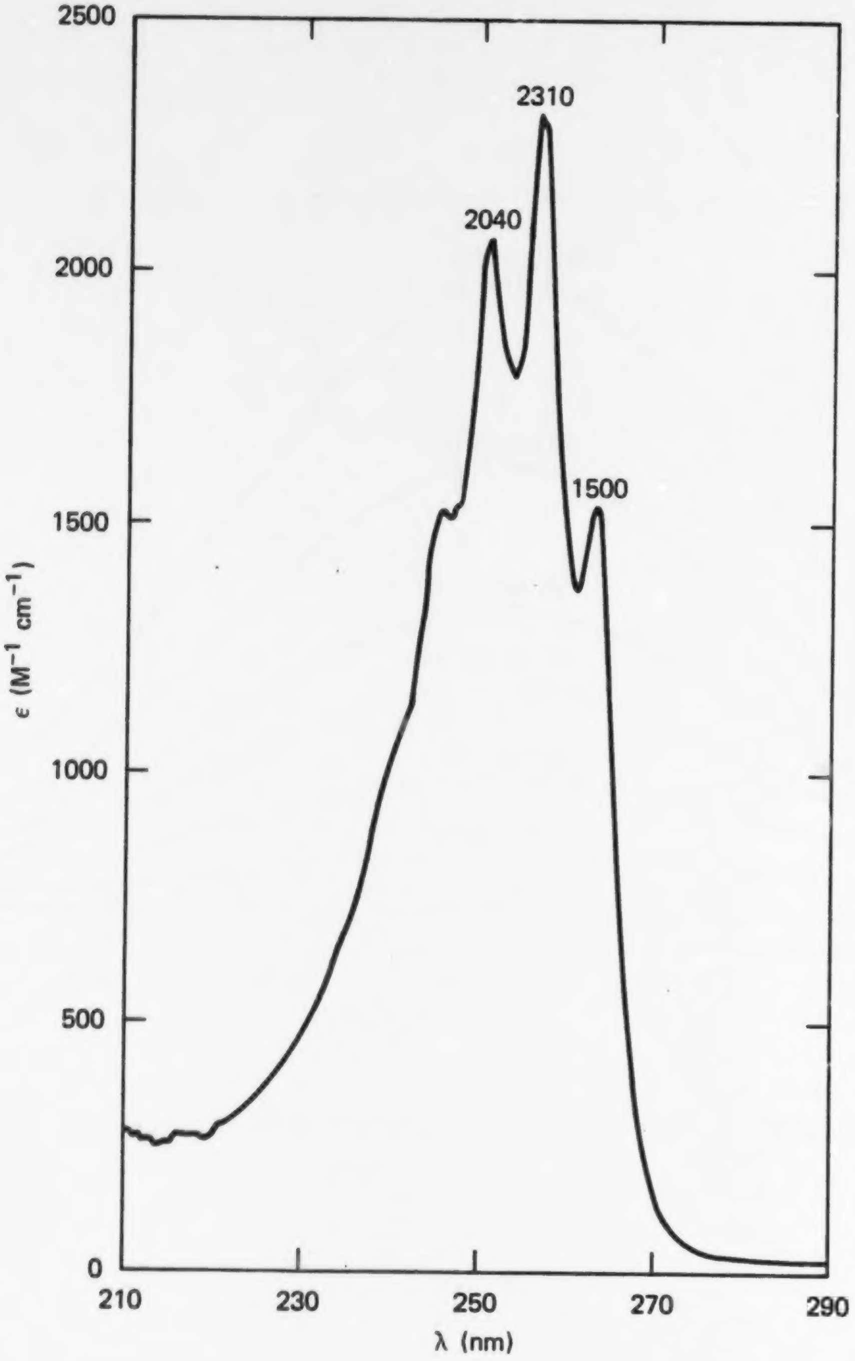

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Figure 6.2 UV spectrum of pyridine in methanol.

energy, giving the spectrum shown in Figure 6.3 with an ε of 5,700 L $M^{-1}cm^{-1}$ at 257 nm. Thus, a spectrophotometric analysis based on this UV band should provide approximately a three-fold increase in sensitivity compared with the standard analysis at 407 nm.

This rather modest increase in sensitivity would not by itself extend the range of the method down to the desired limit of 2 ppb SCN^-. Other shortcomings of the method include: (1) increased sample handling necessary to remove the chloroform and excess pyridine extracted into the chloroform, (2) instability of this complex in the absence of excess pyridine.

An obvious way to increase the lower limit of detection of this method is to use an aromatic amine whose extinction coefficient is much greater than pyridine. Unfortunately, the coextraction of excess nonvolatile ligand into the chloroform along with the copper complex was a recurring problem. The UV bands are not shifted enough by complexation to permit one to distinguish between free and coordinated ligand. However, high performance liquid chromatography appeared to offer a convenient means of separating the complex from excess ligand and taking full advantage of the more intense absorbance in the UV region of the spectrum.

6.3 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

A high performance liquid chromatographic (HPLC) analysis should separate the copper complex from free ligand, thus allowing quantitative analysis of the complex with a UV detector. In addition, the expanded scale of an HPLC detector system, compared with the 1 absorbance until full-scale recorder on the Cary 14, should increase the apparent sensitivity of the method. Finally, it was considered desirable to investigate the possibility of achieving on-column concentration of the sample by a judicious choice of solvent systems.

Chromatograms were recorded using a Du Pont 848 liquid chromatograph equipped with a variable wavelength model 837 UV-Vis detector with an 8-mm pathlength. Maximum sensitivity was 0.01 AU full scale, although excessive noise limited the useful attenuation to 0.04 AU full scale. Taking into consideration the difference in pathlengths, this represents a twentyfold scale expansion compared to the Cary 14. A series of Waters and Du Pont columns were used with a variety of solvent systems, as described below.

In the initial experiments, a reverse phase system was used, consisting of a nonpolar permaphase ODS column and a polar 80% MeOH/20% H_2O mobile phase. The choice of solvents was based on the relatively high solubility of the $Cu(Py)_2(SCN^-)_2$ complex in this solvent system. Typical chromatograms are shown in Figure 6.4. Injection of a methanolic solution of the copper complex resulted in a solvent peak at 1.1 min, followed closely by a pyridine peak at 1.3 min. No peak was observed that could be assigned to the copper complex. Since the original sample contained no excess pyridine, the detection of the free ligand in the analysis indicated that the copper complex was at least partially dissociated in this solvent system.

The dissociation of the copper complex was confirmed by recording the visible spectrum of $Cu(Py)_2(SCN^-)_2$ in pure methanol and in an 80% MeOH/20% H_2O

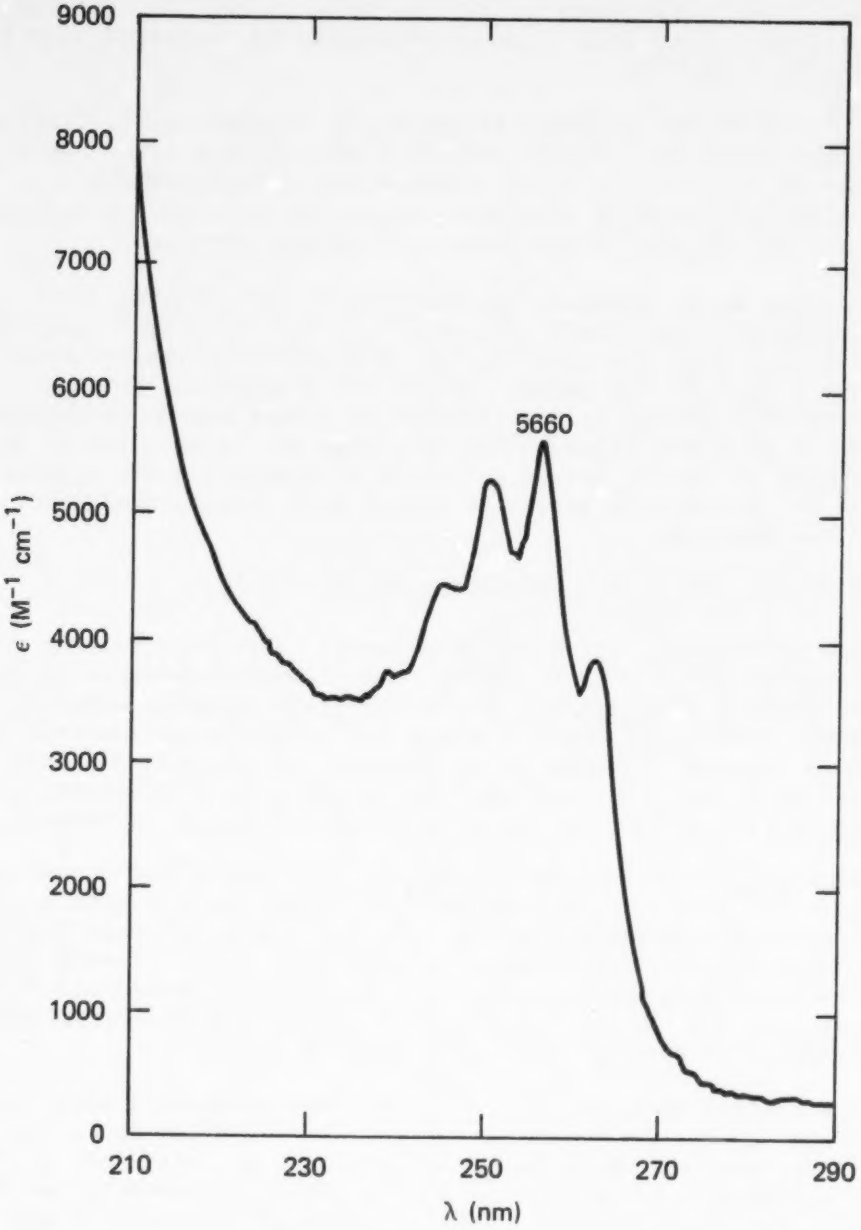

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Figure 6.3 UV spectrum of dithiocyanatodipyridylcopper(II) complex in methanol.

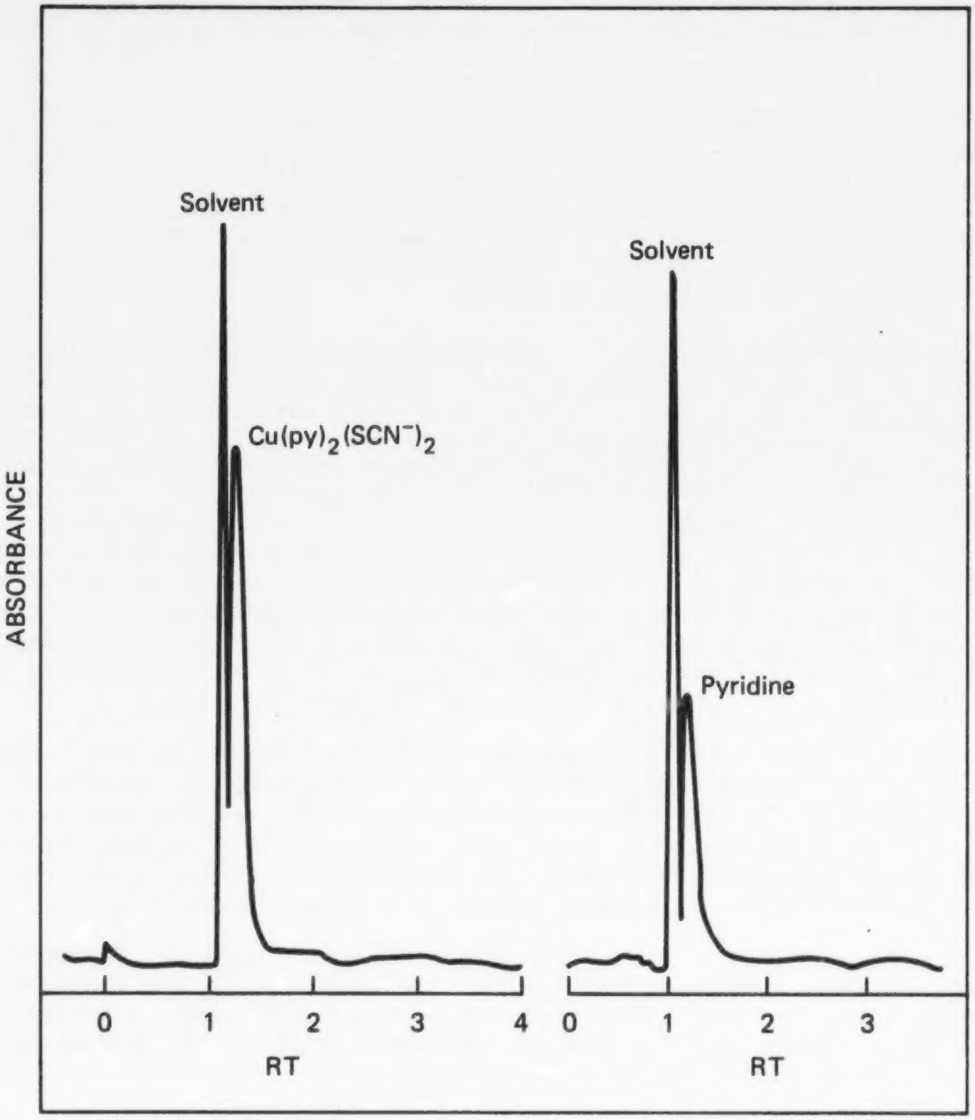

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Figure 6.4 HPLC chromatograms of the dithiocyanatodipyridylcopper (II) complex.

Column – permaphase ODS
Flow Rate – 1.25
Solvent – 80% methanol, 20% water
Sample Size – 50
Detector wavelength -260 nm
Samples dissolved in methanol

mixture, as shown in Figure 6.5. Curve 1 represents the intact complex in methanol, while Curve 2 shows the spectrum resulting from a 25% dilution with H_2O. Instead of a straightforward reduction in absorbance due to dilution, there is a 70% decrease in absorbance at 390 nm and a shift in λ_{max} to shorter wavelengths.

Further study revealed that even in pure methanol there is a slow decrease in absorbance, with approximately a 20% loss in intensity over the first 1-1/2 hours. Presumably, the solvent is displacing pyridine from the inner coordination sphere of the copper. In the absence of any coordinated amines, cupric ion in the presence of thiocyanate is unstable with respect to reduction to cuprous ion. Since the cuprous complex lacks any charge transfer spectrum, there is a decrease in absorbance at 390 nm.

The second HPLC analysis was performed with a bondapak C18 column. Chloroform was chosen as the solvent, since previous workers had established that the copper complex is stable in this solvent in the presence of excess pyridine.[30] Pyridine itself elutes from this column with a retention time of 16.5 min. A solution of $Cu(Py)_2(SCN^-)_2$ dissolved in a pyridine/$CHCl_3$ mixed solvent gives only a single peak at 16.5 min. The addition of more solid $Cu(Py)_2(SCN^-)_2$ to the sample solution caused a steady increase and slight shifting of this band to ∿15.5 min, as shown in Figure 6.6, but no additional peaks were observed. The coelution of the complex and pyridine was ruled out on the basis of the chromatogram of the most concentrated copper solution, with the detector set to the 407 nm λ_{max} of the complex. No peaks were observed, indicating that the increase in the 16.5 min peak observed with the detector at 260 nm is due to free pyridine.

Our experience tends to corroborate previous reports that the copper complex is stable in a pyridine/$CHCl_3$ solvent. The apparent decomposition of this complex during HPLC analysis could be due to strong interactions of cupric ion with the column packing. Alternatively, excess pyridine may be a necessary factor for long-term stability. Thus, the on-column separation of the complex from free pyridine may lead to dissociation of coordinated pyridine.

These results do not prove that the complex is completely dissociated during the analysis. Because of the rather low solubility of the copper complex in pure chloroform, it is possible that the separation of excess pyridine could also lead to on-column precipitation of the intact complex. No quantitative data are available from which to estimate the percent of dissociation versus precipitation.

The direct analysis of $Cu(Py)_2(SCN^-)_2$ by liquid-solid chromatography has also been investigated with a Waters' porasil column and 1:1 THF/$CHCl_3$ as the mobile phase. Injection of pyridine dissolved in the mobile phase resulted in a peak at 7 min that tailed somewhat, presumably because of interaction of the basic pyridine nitrogen with the acidic column material. Injection of $Cu(Py)_2(SCN^-)_2$ dissolved in 1:1 THF/$CHCl_3$ produced no peaks at all. Switching to a 50:50:1 dioxane/$CHCl_3$/isopropanol mobile phase produced the same results. Injection of the copper complex dissolved directly into the mobile phase with no excess pyridine resulted in a blank chromatogram, with no peak for either the complex or free pyridine. The retention time for pyridine was determined to

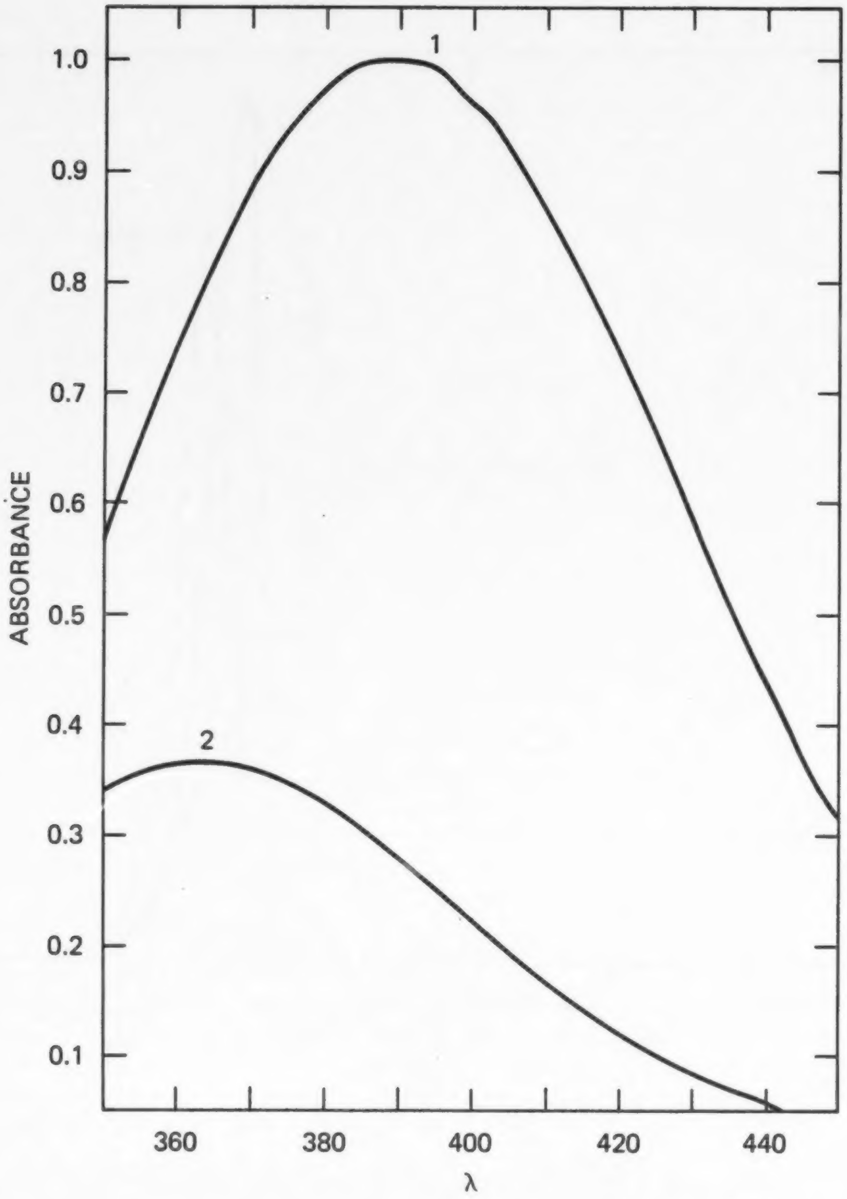

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Figure 6.5 Absorption spectra of the dithiocyanatodipyridylcopper (II) complex in (1) methanol, and (2) 20 mL methanol and 5 mL water.

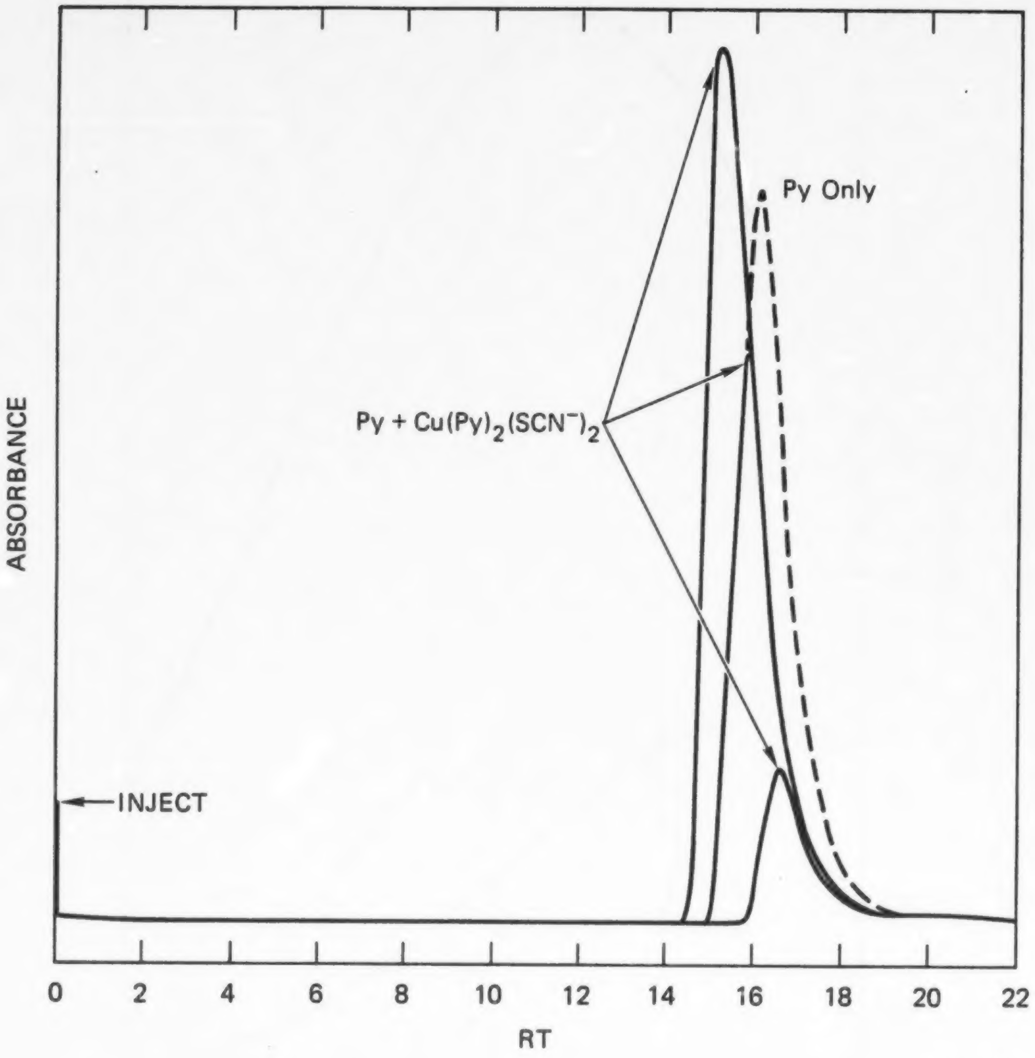

Figure 6.6 HPLC chromatograms of the dithiocvanatodipyridylcopper (II).

Column – Bondapak C18
Sample Size – 20
Flow Rate – 1
Solvent System – Chloroform
Detector Wavelength – 260 nm

be 10 min by the separate injection of pyridine alone. Finally, pure chloroform was used as the mobile phase, but it, too, failed to elute the copper complex from the porasil column.

Because of the continuing difficulties in the analysis of $Cu(Py)_2(SCN^-)_2$, a new ligand, 1,10-phenanthroline, was substituted for pyridine. The choice of this ligand was based on two factors. First, because it is bidentate, it forms much more stable copper complexes than does pyridine, and thus is less likely to dissociate from the metal ion under very dilute conditions. In addition, phenanthroline has a very intense absorption band at 265 nm, as shown in Figure 6.7, with an ε of 28,000 $LM^{-1}\ cm^{-1}$, which should increase the sensitivity with a UV detector.

The addition of KSCN to a 1:1 solution of copper and phenanthroline resulted in the immediate precipitation of the green mixed-ligand complex. However, unlike the bis(pyridine) analogue, the phenanthroline complex is virtually insoluble in all common organic solvents. Thus, because it is not possible to use the routine extraction into chloroform, the initial extraction of SCN^- from water was performed in the normal manner using pyridine. The chloroform layer was then re-extracted with an aqueous solution of phenanthroline, resulting in the formation of the blue $Cu(phen)_2^{2+}$ complex in the aqueous layer. The absorption spectrum of this complex is also shown in Figure 6.7. Based on an ε per copper of 58,000 $M^{-1}cm^{-1}$, there is a potential thirtyfold increase in sensitivity compared to the 407 nm band of $Cu(Py)_2(SCN^-)_2$.

Unlike the neutral $Cu(Py)_2(SCN^-)_2$ complex, $Cu(phen)_2^{2+}$ is a divalent cation so that different strategies apply to its analysis by HPLC. The primary goal was the separation of the $Cu(phen)_2^{2+}$ complex from excess phenanthroline. The most obvious approach was to use a reverse phase system that would retard the hydrophobic ligand but would not interact strongly with the charged copper complex. However, the injection of an aqueous solution of $Cu(phen)_2(NO_3)_2$ onto a bondapak ODS column with a methanol mobile phase resulted in no peaks. Further investigation revealed that phenanthroline itself was not eluted from this column by methanol, even though pyridine was observed in 5 min. The effect of increased molecular weight on retention time was estimated by injecting anthracene, which was easily detected by 5.5 min. Thus, the larger molecular weight of phenanthroline does not account for its strong retention by this column. Further attempts to elute the $Cu(phen)_2^{2+}$ complex using 20% MeOH/80% 0.01 phosphate buffer at pH 7 were also unsuccessful. Ion pair chromatography was also investigated as a technique for analysis of the bis(phenanthroline) copper(II) complex. The commercial reagent PIC B5 (n-pentanesulfonic acid) was added to the methanol-phosphate mobile phase, and the pH was readjusted to 7.0. The anionic sulfonate groups should form ion pairs with the cationic copper complex. It was hoped that this neutral species could then be eluted from a reverse phase column--in this case, permaphase ODS. Unfortunately, this was not the case, and neither the copper complex nor free phenanthroline could be eluted from the column with this system.

The final attempt to analyze for the copper-phenanthroline complex involved ion exchange chromatography using a Du Pont Zipax-SCX strong cation exchange column, with a pH 9.5 borate buffer as the mobile phase. However, as in the previous methods, neither the free ligand nor the copper complex eluted from the column. This column also retained a sample of bis(ethylenediamine)copper(II).

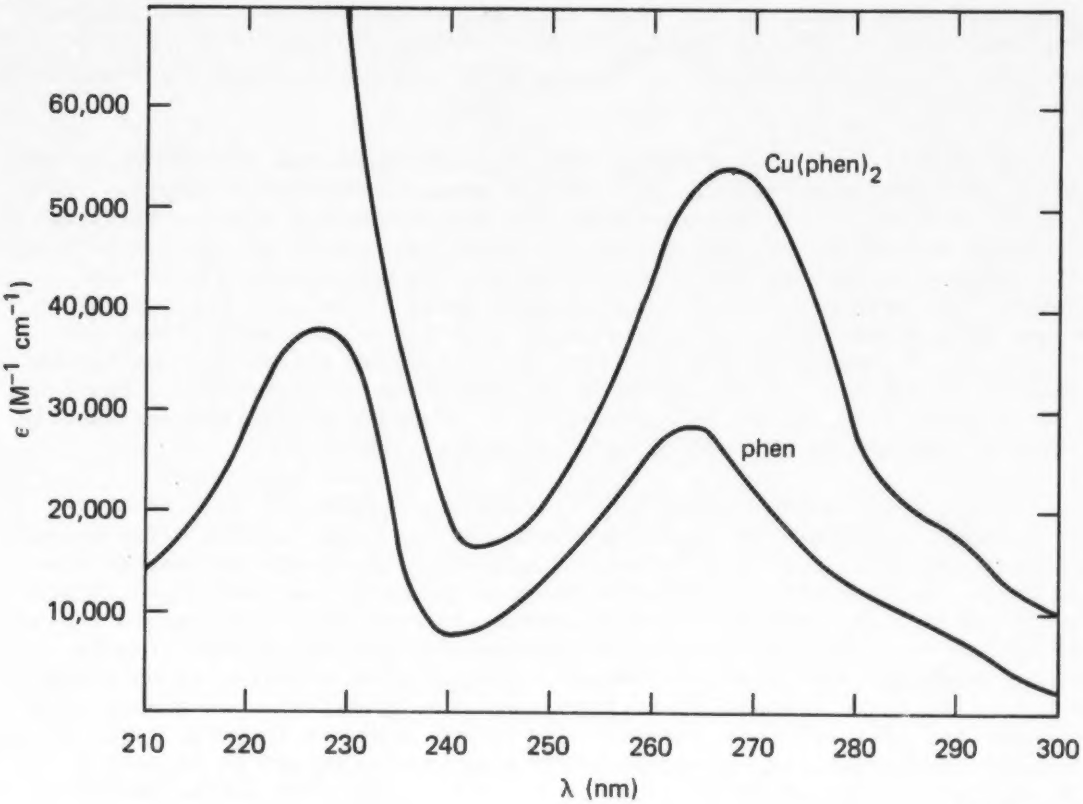

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Figure 6.7 Spectra of Cu(phen)$_2$ and phenanthroline in water.

Thus, there appeared to be two problems: (1) some unexpected interaction of phenanthroline itself with the packing material, which may be decomposing the copper complex, and (2) very strong retention of divalent cations.

An obvious, recurring problem in the analysis of phenanthroline complexes is the strong interaction of the free ligand with the packing materials. Thus, phenanthroline does not appear to be a suitable ligand, despite its strong sequestering abilities and attractive uv spectrum. There are still other ligands that might merit future consideration, such as the β-diketonates and β-ketoamines, which have been used previously to obtain analyses of various metal ions, as well as the ethylene-bis-(salicylaldimines) (salen) ligands, which have not been used in this capacity. However, any future programs must take into consideration some serious problems recently discovered in the chloroform extraction of the pyridine complex. These are discussed in detail in the following section on atomic absorption spectroscopy.

6.4 ATOMIC ABSORPTION SPECTROSCOPY

In the proposed ASTM Method B,[32] cupric nitrate and pyridine are added to a thiocyanate sample, and this aqueous solution is extracted with $CHCl_3$. The SCN^- is quantitatively transferred to the chloroform layer as the $Cu(Py)_2(SCN^-)_2$ complex. Next, the $CHCl_3$ is removed and the copper complex is redissolved in ethyl acetate. This solution is then analyzed by flame atomic absorption spectroscopy. The method is used when the original SCN^- sample is in the 0.05-2.0 ppm concentration range.

A revised method that uses graphite furnace atomic absorption instead of flame atomic absorption was studied. It was anticipated that this modification would have two beneficial effects. One, the sample could be analyzed directly in the $CHCl_3$ matrix, eliminating the time-consuming change in solvent. More important, however, is the greater sensitivity of graphite furnace AA, which can detect copper in the low ppb range.

Data were collected using a Varian AA6 spectrometer equipped with a graphite furnace attachment and 20-mL carbon rods. The program consisted of drying at 100°C for 40 sec, ashing at 700°C for 20 sec, and atomization at 2200°C for 2 sec. The ramp rate was 600°C/sec. Samples of 4-8 mL were slowly injected after the carbon rod had reached the 100°C drying temperature to prevent the chloroform from creeping out the ends of the tube. To keep the spectrometer reading on-scale over the wide range of concentrations studied, it was necessary to use different sample volumes. The reported intensities are normalized according to the equation

$$\text{Intensity} = \frac{\text{Absorbance}}{\text{Volume Injected}} \times 1000$$

which gives intensity values in the general range of 1-200.

A bulk sample of $Cu(Py)_2(SCN^-)_2$ was prepared by adding 0.483 g KSCN (5 mmol) dissolved in a minimum volume of water to a 50-mL aqueous solution of 0.483 g $CuCl_2$ (2.8 mmol) and 3 mL of pyridine. This resulted in the immediate precipitation of a dark-green powder, which was filtered from solution, washed with water, and air-dried.

The copper content of this material was determined by weighing 20-30 mg samples into 50-mL beakers, then covering and gently heating them for 2 hours in ∿10 mL concentrated HNO_3. These solutions were then quantitatively transferred to 50-mL volumetric flasks and diluted to volume with distilled water, giving solutions with copper concentrations in the 4-8 ppm range, which were then analyzed by flame AA using commercial copper standards. An average value of 21.5 ± 0.4% copper by weight was obtained for four samples (calculated for $CuC_{12}H_{10}N_2S_2$ = 20.5%.)

A carefully weighed sample of $Cu(Py)_2(SCN^-)_2$ was dissolved in 100 mL of 95% $CHCl_3$/5% pyridine solvent to give a stock solution that contained 21.6 μg Cu/ml. Thereafter, daily calibration curves were prepared by first diluting this stock solution 1:100 with pyridine/$CHCl_3$ to give a solution containing 0.216 μg Cu/ml. This dilute solution was then used to prepare a series of standards needed to construct a calibration curve such as the one in Figure 6.8. The slopes of these curves were fairly constant for 1 day. However, the intercepts tended to drift, so that it was necessary to frequently recalibrate the instrument during the analysis of several unknowns.

Based on the slope of the calibration curve and the observed reproducibility of the spectrometer readings, one should be able to detect ∿15 ppb copper. This corresponds to 8 ppb SCN^- in the original aqueous solution. Initial efforts to extract SCN^- from aqueous solutions and analyze the $CHCl_3$ layer by this method gave very erratic results. The background level of copper being extracted into the $CHCl_3$ was determined by using 10 mL of $CHCl_3$ to extract samples of 0.00262 M $Cu(NO_3)_2$ containing various amounts of pyridine but no thiocyanate. The results are shown in Table 6.1.

TABLE 6.1 EXTRACTION OF COPPER-PYRIDINE SOLUTIONS WITH CHLOROFORM IN THE ABSENCE OF THIOCYANATE

Sample No.	ml Pyridine	AA Intensity	ppb Cu (est.)
1	1.0	137 ± 8	188 ± 12
2	1.0	150 ± 5	200 ± 8
3	1.0	125 ± 6	162 ± 9
4	1.0	182 ± 6	249 ± 9
5	0.5	63 ± 7	66 ± 11
6	0.5	69 ± 2	76 ± 4

Intensity = 0.65 (ppb Cu) + 19.9

Clearly, it is not possible to obtain accurate low ppb analyses when the background fluctuates from 150-250 ppb, with an average of 200 ± 40 ppb Cu. It

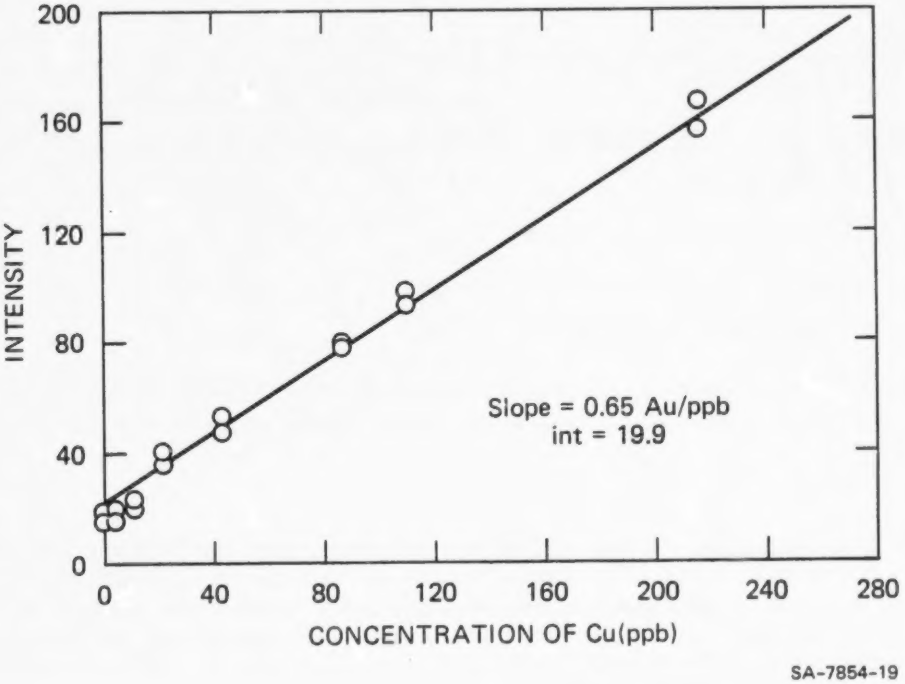


Figure 6.8 Graphite furnace calibration curve of dithiocyanatodipyridylcopper(II).

would be necessary to have at least 80 ppb copper just to be significantly above the noise level. This corresponds to 73 ppb SCN^- as the $Cu(Py)_2(SCN^-)_2$ complex.

The results for samples 5 and 6 clearly establish a correlation between the background copper level and the concentration of pyridine in the aqueous layer. An effort was made to reduce the background copper to an acceptable level by extracting 25-mL samples of 101 ppb SCN^- following the addition of only 0.5 mL pyridine and various amounts of copper. These results are shown in Table 6.2.

TABLE 6.2 EXTRACTION EFFICIENCY OF DITHIOCYANATODIPYRIDYLCOPPER(II) BY CHLOROFORM

	ppb Cu in 10 mL $CHCl_3$		
Aqueous Copper Concentration	0.00262 M	0.00116 M	0.00604 M
First 10-mL extract	131	82	57
blank	71	38	32
net	60	44	25
% recovery of SCN^-[a]	48%	35%	20%
Second extraction (ppb Cu)	20	19	20

[a] Calculated assuming all copper in first 10-mL extract was $Cu(Py)_2(SCN^-)_2$.

The results indicate that adding 0.5 mL of pyridine does not result in complete extraction of the SCN^-, and that any attempts to reduce background levels by reducing the initial copper concentration also have an adverse effect on the extraction efficiency. Multiple extractions are of limited use in obtaining complete extraction of the copper complex due to the almost complete removal of free pyridine in the initial 10-mL extraction.

Despite the low recovery of SCN^-, an attempt was made to obtain a calibration curve by extracting a series of standard KSCN solutions using 0.00116 M copper and 0.5 mL pyridine. However, the points were widely scattered and indicated that although the level of 38 ppb Cu reported in Table 6.2 is close to the average, the individual background levels range from 20 to 70 ppb. Any further reduction in copper or pyridine concentrations does not appear to be reasonable in light of the already low extraction efficiency for SCN^-.

The results discussed above all indicate that standard extraction procedures simply are not acceptable for use with thiocyanate at the low ppb level. Although it is still not known exactly what species are being extracted into chloroform, there is clearly at least one copper-pyridine complex that is slightly soluble in $CHCl_3$. Pyridine itself is very soluble in chloroform. It was felt that by adding substituents to pyridine that reduce its extraction coefficient, one might also impede the extraction of its copper complexes as well. Thus, 50-mL aliquots of 0.00143 M copper solution were extracted with 10 mL of $CHCl_3$ after the addition of 12.4 mmoles of the appropriate pyridyl ligand (L/Cu = 170) but no thiocyanate. The results are shown in Table 6.3.

TABLE 6.3[a] EXTRACTION OF CUPRIC ION BY PYRIDYL LIGANDS IN THE ABSENCE OF THIOCYANATE

Ligand	ppb Copper
Pyridine	350
2-Aminopyridine	580
3,5-Dichloropyridine	160
2-Hydroxy-5-nitropyridine[b]	-
2,6-Diaminopyridine	660

[a] 50 mL of 1.43 MM $Cu(NO_3)_2$ extracted into 10 mL $CHCl_3$ in the presence of 12.4 mmoles of ligand.

[b] This ligand is virtually insoluble in water.

Both the 2,6-diaminopyridine and 3,5-dichloropyridine are difficult to work with because of their limited water solubility. A large portion of each of these ligands failed to dissolve in the original 50-mL aqueous layer, but the solid 3,5-dichloropyridine did dissolve in the chloroform layer. The 2-hydroxy-5-nitropyridine was so insoluble in water that no analysis of the chloroform layer was conducted. It is obvious that none of the substituted pyridines are capable of reducing the copper background to an acceptable level.

Since the atomic absorption method does not depend on the intense color associated with the pyridine complex, aliphatic amines were also considered as extracting agents. The usual extraction procedure was followed using the amines listed in Table 6.4.

TABLE 6.4 COPPER EXTRACTED BY ALIPHATIC AMINES AT pH 7

		ppb Cu Extracted[a]		
Ligand	ppb SCN	Cu + SCN	Cu only	Net
NH_3[b]	327	8	4	4
n-Butylamine[c]	503	42	32	10
Diethylamine[c]	503	10	7	3
Triethylamine[c]	503	14	18	-3

[a] 50-mL samples; 0.00135 M $Cu(NO_3)_2$.

[b] Added 0.9 mL concentration NH_4OH.

[c] Added 2.0 mL neat amine.

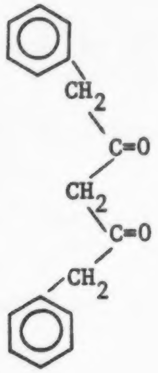
Although these ligands were very successful in reducing the copper background to an acceptable level, they do not facilitate the extraction of thiocyanate into the organic layer. The color of these solutions at pH 7 is quite pale compared to their intense blue color at higher pH. Thus, it is not clear whether their failure to extract SCN^- is due to a low distribution coefficient of the $Cu(SCN^-)_2(amine)_2$ complex or to the low degree of formation of such a complex.

6.5 CONCLUSIONS AND RECOMMENDATIONS

Thiocyanate can be readily removed from the sample matrix by extraction of the $Cu(Py)_2(SCN^-)_2$ complex. The copper can be quantitated by atomic absorption, and the concentration of SCN^- can be determined using the 2:1 stoichiometric ratio of SCN^-:Cu. Carbon rod AA analysis of copper is sufficiently sensitive to permit quantitation of SCN^- at 2 ppb if one can obtain a two- to threefold concentration in the extraction step. However, the excess pyridine extracts additional copper in addition to that bound to thiocyanate. This simultaneous extraction of excess copper must be drastically reduced, and this appears to be a formidable task. Any ligand that forms an extractable mixed-ligand complex with copper thiocyanate is also likely to form soluble binary copper complexes as well. Thus, it is necessary to find a ligand that will extract the thiocyanate complex but still give a low background of copper.

The results presented above indicate that pyridine derivatives are not suitable for SCN^- extractions at low levels. Although the results for the aliphatic amines are not particularly encouraging, to date there has been no systematic investigation of the effects of pH on this process. One can continuously vary the effective binding constant of these amines by varying the pH. A multitude of other compounds also deserve consideration, such as substituted bidentate diamines, aniline derivatives, or imidazole derivatives. Other solvents may also be considered. It is probable, however, that any program intended to optimize an extraction procedure adaptable to a low ppb SCN^- analysis will require a considerable level of effort.

An improvement of the HPLC method of analysis also requires a suitable extraction procedure to separate the SCN^- from the sample matrix. Assuming such a procedure is developed, HPLC still has high potential as a method of quantitating SCN^-. The best approach is to react the extracted mixed-ligand complex with a suitable multidentate ligand to form a stable, easily detected copper complex. This was the approach taken here using phenanthroline, which appears to be an unfortunate choice because of its unexpected interaction with the packing materials. However, a number of other ligands could be useful, such as those shown below.



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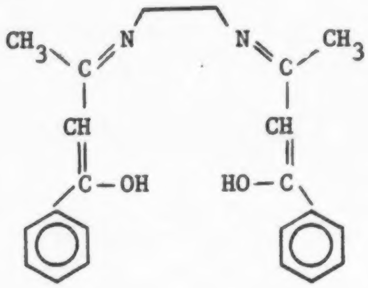

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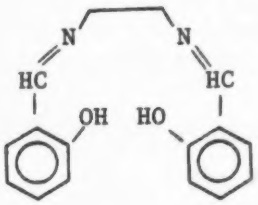

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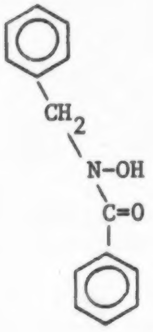

IV

Ligands I-IV all form neutral complexes with cupric ion. In addition, it is fairly straightforward to add substituents to the aromatic rings so as to alter the solubility of the complex as needed and also to increase the absorptivity in the uv region; the latter would serve as a convenient basis for detection.

Another method that offers the possibility of direct analysis of SCN^- without an extraction step is ion chromatography. Because of its size, SCN^- is strongly retained on most columns and thus easily separated from common anions such as Cl^-, Br^-, and No_3^-. By use of a precolumn, significant concentration of the sample is possible. This technique has allowed analysis of Cl^- at the 5-ppb level.[32] To alleviate the interferences from metal ions, a suitable chelating agent could be added to sequester the metals and free coordinated SCN^-. The most likely choices would be polyamines, since they are cations at neutral pH and thus would not be retained by the column.

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Appendix A

EDTA AERATION PROCEDURE FOR SIMPLE CYANIDES

1. Scope and Application

1.1 This method is applicable to the determination of cyanides in drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/L (0.1 mg/100mL of absorbing liquid).

1.3 The colorimetric procedure is used for concentrations below 1 mg/mL and is sensitive to about 0.02 mg/L.

1.4 The potentiometric procedure is used for concentrations between 26 and 0.02 mg/L. The lower limit can be extended through the use of a calibration curve to 0.002 mg/L. Higher concentrations can be measured but since these cause increased erosion of the membrane, measurements above 26 mg/L cyanide should be done only occasionally.

2. Summary of method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide compounds by means of a 2-hour aeration in the presence of EDTA at pH 4.5. The cyanide so released is absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is quantitated volumetrically, colorimetrically, or electrometrically.

2.2 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

2.3 In the colorimetric measurement the cyanide is converted to cyanogen chloride (CNCl) by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of a pyridine-pyrazalone or a pyridine-barbituric acid reagent. The absorbance of the resulting colored solution is read at 620 nm when using pyridine-pyrazalone and 578 nm when using the pyridine-barbituric acid reagent. It is essential to have comparable ionic strenghs in both the sample and the standards.

2.4 The potentiometric measurement uses a cyanide ion selective electrode and double junction reference electrode to quantitate the cyanide ion. It is essential that both the sample and the standard have comparable ionic strengths.

3. Definitions

Simple cyanides in this method are defined as cyanide ion and easily dissociated complex cyanide converted to hydrocyanic acid by reaction in an aeration system of an acetate buffer in the presence of EDTA.

4. Sample handling and preservation

4.1 The sample should be collected in plastic or glass bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and rinsed to remove soluble material.

4.2 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Add an additional 0.6 g ascorbic acid for each liter of sample volume.

4.3 Sulfides slowly convert the cyanide in the sample to thiocyanate. The reaction rate is greatly increased at high pH. Sulfide therefore interferes and should be removed as soon as the sample is collected and before adjustment of the pH. When sulfides are present in the sample, it may be assumed that oxidizing agents are absent. Test for the presence of sulfide by placing a drop of the sample on a strip of lead acetate test paper that has been previously moistened with the acetic acid solution. Darkening of the test paper indicates the presence of sulfide.

4.3.1 Sulfide is removed by treating the sample with small increments of powdered lead carbonate ($PbCO_3$), cadmium carbonate ($CdCO_3$), or with the dropwise addition of lead nitrate [$Pb(NO_3)_2$] solution. (When significant quantities of sulfide must be removed, the addition of $PbCO_3$, or $CdCO_3$ is preferred. $Pb(NO_3)_2$ may unduly depress the pH, and with $Pb(OAc)_2$ additions, the acetic acid that distills over may neutralize too much NaOH in the absorber). Black PbS precipitates in samples containing sulfide. Repeat the operation until no more lead sulfide forms, as indicated by testing the supernatant liquid with $Pb(OAc)_2$ test paper. It is not necessary to filter the sample because $S^{=}$, as PbS, does not interfere.

4.4 Samples must be preserved with 2 mL of 10N sodium hydroxide per liter of sample (pH 12) at the time of sample collection. (Additional base may be necessary to ensure that the pH of the sample is ≥12.)

4.5 Samples should be analyzed as soon as possible. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain the temperature at 4°C.

4.6 Minimize exposure of the samples to ultraviolet radiation. Photodecomposition of the iron cyanides may significantly increase the cyanide content of the sample. (Remove interferences in the hood under incandescent light conditions, etc.)

5. Interferences

5.1 Interferences are eliminated or reduced by using the aeration procedure described in Sections 8.1 and 8.7.

5.2 Organic thiocyanates will be transferred to the scrubber solution by the air stream. These compounds adversely affect quantitation by electrochemical means. (It may be possible to remove these compounds from the sample prior to aeration by the extraction procedure described for fatty acid removal.)

5.3 Aldehydes react with cyanide to produce nitriles under the analysis conditions. These nitriles are further hydrolyzed to their corresponding acid and ammonia.

5.4 The presence of heavy metals (e.g., Hg^{++}) inhibit the transfer of cyanide to the scrubber solution by forming stable mercury-cyanide compounds.

5.5 Other possible interferences include substances that might otherwise contribute color or turbidity. In most cases, the aeration procedure will remove these.

6. Apparatus

6.1 The aeration apparatus is shown in Figure 1.* The boiling flask should be of 1-liter size with an inlet tube and provision for a condenser.

6.2 Microburet, 5.0 mL (for titration).

6.3 Spectrophotometer suitable for measurement at 578 nm or 620 nm with a 1.0 cm cell or larger.

6.4 A cyanide ion selective electrode, a double junction reference electrode, an expanded scale mV meter or specific ion meter, and a magnetic mixer with TFE fluorocarbon-coated stirring bar.

7. Reagents

7.1 Sodium hydroxide solution, 1.25 N: Dissolve 50 g NaOH in distilled water and dilute to 1 liter with distilled water.

7.2 Cadmium carbonate: Powdered.

7.3 Ascorbic acid: Crystals.

7.4 Dilute sodium hydroxide solution, 0.25 N: Dilute 200 mL of sodium hydroxide solution (7.1) to 1 liter with distilled water.

7.5 Methyl red indicator: Prepared as 0.02 g in 60 mL H_2O and 40 mL acetic acid.

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*Figure 1 is given at the end of the Appendix.

7.6 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g $NaH_2PO_4 \cdot H_2O$ in 1 liter of distilled water. Refrigerate this solution.

7.7 Stock cyanide solution, 1 mg/mL: Dissolve 2.51 g KCN and 2 g KOH in 1 liter distilled water. Standardize with 0.0192N $AgNO_3$. Dilute to appropriate concentration so that 1 mL = 1 mg CN^-.

7.8 Standard cyanide solution, intermediate, 50 mg/L: Dilute 50.0 mL of stock solution (7.7) to 1 liter with distilled water.

7.9 Standard cyanide solution, 5 mg/L: Prepare fresh daily by diluting 100.0 mL of intermediate solution (7.8) to 1 liter with distilled water and store in a glass-stoppered bottle.

7.10 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g dried $AgNO_3$, dissolve in distilled water, and dilute to 1 liter (1 mL = 1 mg CN^-).

7.11 Rhodanine indicator: Dissolve 20 mg p-dimethylaminobenzalrhodanine in 100 mL of acetone.

7.12 Chloramine-T solution: Dissolve 1 g of white, water-soluble chloramine-T in 100 mL of distilled water and refrigerate until ready to use. Prepare fresh weekly.

7.13 Color reagent - One of the following may be used:

7.13.1 Pyridine-barbituric acid: Place 15 g of barbituric acid in a 250-mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of HCl (sp gr 1.19); mix and cool to room temperature. Dilute to 250 mL with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.13.2 Pyridine-pyrazolone solution:

7.13.2.1 3-methyl-1-phenyl-2-pyrazolin-5-one reagent saturated solution: Add 0.25 g of this compound to a 50 mL distilled water; heat to 60°C with stirring. Cool to room temperature.

7.13.2.2 3,3'-dimethyl-1,1'-dipenyl-(4,4'-bi-2-pyrazoline)-5,5'-dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 mL pyridine.

7.13.2.3 Pour solution (7.13.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter pour solution (7.13.2.2), collecting the filtrate in the same container as the filtrate from (7.13.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but does not affect the color production with cyanide if used within 24 hours of preparation.

7.14 Acetate buffer solution: Dissolve 410 g sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) in 500 mL of water. Add glacial acetic acid to pH 4.5, approximately 500 mL.

7.15 EDTA solution: Dissolve 66 g disodium(ethylenedinitrilo)tetraacetate dihydrate ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$) in 1 liter water.

8. Procedure

8.1 Place 500 mL of sample, or an aliquot diluted to 500 mL , in the 1-liter boiling flask. Add 50 mL of sodium hydroxide (7.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the vacuum train.

8.2 Turn on the vacuum and adjust the air flow rate through the flask to approximately 3 liters per minute or greater.

8.3 Add 2-3 drops of the methyl red indicator to the reaction flask.

8.4 Add 10 mL each of the acetate buffer (7.14) and EDTA solutions (7.15) through the air inlet tube.

8.5 Rinse the air inlet tube with a few ml of water and allow the air flow to mix with the contents of the flask. (If the solution is not pink, add acetic acid dropwise through the air inlet tube until there is a permanent color change.)

8.6 Allow the air to flow through the sample for 2 hours at the rate of at least 3 liters per minute. (Do not heat the sample.)

8.7 After 2 hours, stop the air flow and quantitatively transfer the absorption liquid to a 250-mL volumetric flask.

8.8 This solution, or an aliquot of this solution, is then analyzed for cyanide using the colorimetric, titrimetric, or potentiometric method of analysis.

8.9 Titrimetric method of analysis

8.9.1 If the sample contains more than 1 mg of CN^-, transfer the distillate, or a suitable aliquot diluted to 250 mL to a 500-mL Erlenmeyer flask. Add 10-12 drops of the rhodanine indicator (7.11).

8.9.2 Titrate with standard silver nitrate (7.10) to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.9.3 The analyst should familiarize himself (herself) with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 mL microburet may be conveniently used to obtain a more precise titration.

8.10 Colorimetric method of analysis

8.10.1 Withdraw 50 mL or less of the solution from the flask and transfer to a 100-mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25 N sodium hydroxide (7.4). Add 15 mL of sodium phosphate solution (7.6) and mix.

8.10.1.1 Pyridine-barbituric acid method: Add 2 mL of chloramine-T (7.12) and mix. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (7.13.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development and then read absorbance at 578 nm in a 1-cm cell within 15 minutes.

8.10.1.2 Pyridine-pyrazolone method: Add 0.5 mL chloramine-T (7.12) and mix. After 1 to 2 minutes add 5 mL of pyridine-pyrazolone solution (7.13.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes read the absorbance at 620 mn in a 1-cm cell. NOTE: More than 0.5 mL chloramine-T will prevent the color from developing with pyridine-pyrazolone.

8.10.2 Prepare a series of standards by pipetting suitable volumes of standard solution into 250-mL volumetric flasks. To each standard add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with distilled water. Prepare as follows:

mL of Standard Solution (5 μg/mL CN^-)	Concentration CN^- (mg CN^-/250 mL)
0	blank
1	0.005
2.0	0.010
5.0	0.025
10.0	0.050
15.0	0.075
20.0	0.100

8.10.2.1 Prepare a standard curve by plotting absorbance of standard versus cyanide concentration.

8.10.2.2 It is not necessary that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within ±10% of the undistilled standards, the operator should find the cause of the apparent error before proceeding.

8.10.3 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to ensure a level of 20 µg/L or a significant increase in absorbance value. Proceed with the analysis as in Section 8.1, using the same flask and system from which the previous sample was just distilled.

8.11 Potentiometric method of analysis

8.11.1 Prepare a series of standards by pipeting suitable volumes of a standard solution into 250-mL volumetric flasks. To each standard add 50 mL of 1.25 N NaOH and dilute to 250 mL with distilled water. Prepare as follows:

mL of Standard Solution	Concentration CN (µg CN^-/250 mL)
(1 µg/mL CN^-)	
2	2
3	3
5	5
10	10
(10 µg/mL CN^-)	
2	20
5	50
10	100
(100 µg/mL CN^-)	
2	200
5	500
10	1000

8.11.1.1 Transfer the standard solutions into 150-mL beakers prerinsed with a small portion of the standard being tested. Immerse the cyanide and double junction reference electrodes in the solution and mix well on a magnetic stirrer. Maintain as closely as possible the same stirring rate and temperature for all solutions.

8.11.1.2 After equilibrium is reached (at least 5 minutes and not more than 10 minutes) record the millivolt reading and plot the CN^- concentrations versus millivolt reading on semilogarithmic graph paper. A straight line with a slope of 59 mV indicates that the instrument is operating properly.

8.11.1.3 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If the distilled standards do not agree within ±10% of the undistilled standards, the operator should find the cause of the apparent error before proceeding.

8.11.2 Place the absorption liquid into a 150-mL beaker and proceed with the analysis as in Section 8.9.1. Determine the CN^- concentration by observing the millivolt reading and referring to the calibration curve established in Section 8.9.1. The method of known addition can be used for measuring occasional samples, since the preparation of a calibration curve is not required.

8.11.3 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to ensure a level of 20 µg/L or a significant increase in values. Proceed with the analysis as in Section 8.1, using the same flask and system from which the previous sample was just distilled.

9. Calculations

9.1 Using the titrimetric procedure, calculate the concentration of CN^- as follows:

$$CN^- \text{ (mg/L)} = \frac{(A-B)(1000)(250)}{(\text{mL of original sample})(\text{mL of aliquot titrated})}$$

where:

A = volume of $AgNO_3$ for titration of sample
B = volume of $AgNO_3$ for titration of blank

9.2 Using the colorimetric procedure, calculate the concentration of CN^- as follows:

$$CN\ (\mu g/L) = \frac{(A)(1000)(250)}{(B)(C)}$$

where:

A = µg CN^- read from standard curve
B = mL of original sample taken for distillation
C = mL of scrubber solution taken for colorimetric analysis.

9.3 Using the potentiometric procedure, calculate the concentration of CN^- as follows:

$$CN^- \ (\mu g/l) = \frac{(A)(1000)(250)}{(B)}$$

where:

A = µg CN read from standard curve
B = mL of original sample taken for analysis

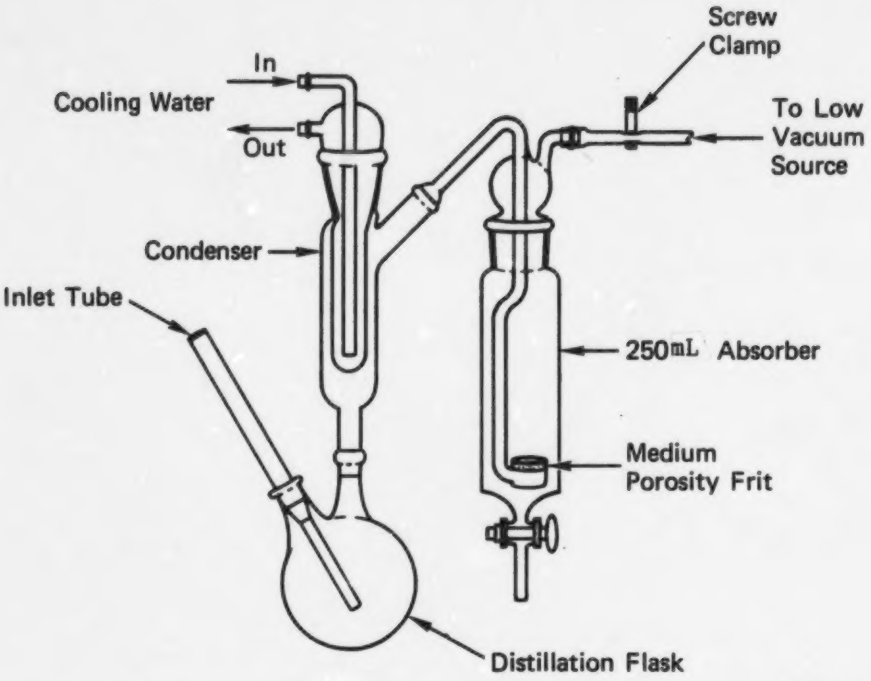
Screw
Clamp
In
Cooling Water
Out
To Low
Vacuum
Source
Condenser
Inlet Tube
250mL Absorber
Medium
Porosity Frit
Distillation Flask
SA-7854-10

Figure 1 AISI AERATION APPARATUS.

Appendix B

MODIFIED ROBERTS-JACKSON METHOD FOR ANALYSIS OF SIMPLE CYANIDES

1. Scope and application

   1.1 This method is applicable to the determination of easily dissociated cyanides in drinking, surface, and saline waters, and domestic and industrial wastes.

   1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/L (0.1 mg/100 mL of absorbing liquid).

   1.3 The colorimetric procedure is used for concentrations below 1 mg/mL and is sensitive to about 0.02 mg/L.

   1.4 The potentiometric procedure is used for concentrations between 26 and 0.02 mg/L. The lower limit can be extended through the use of a calibration curve to 0.002 mg/L. Higher concentrations can be measured, but since these increase erosion of the membrane, measurements above 26 mg/L cyanide should be done only occasionally.

2. Summary of method

   2.1 The method is based on converting to hydrocyanic acid all but the most refactory metal-cyanide complexes from a slightly acidified sample in a 1-hour reflux distillation, and absorbing in a NaOH solution the HCN that has been purged from the sample by an air stream. The procedure avoids the decomposition of iron cyanides that are not amenable to chlorination by omitting the catalyst ($MgCl_2$) and by the addition of zinc and lead acetates which form insoluble double salts with the iron cyanides. The cyanide ion in the absorption solution is quantitated either volumetrically, colorimetrically, or electrometrically.

   2.2 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver-sensitive indicator.

   2.3 In the colorimetric measurement the cyanide is converted to cyanogen chloride (CNCl) by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of a pyridine-pyrazalone or a pyridine-barbituric acid reagent. The absorbance of the resulting colored solution is read at 620 nm when using pyridine-pyrazalone and 578 nm when using the pyridine-barbituric acid reagent. It is essential that both the sample and the standard have comparable ionic strengths.

   2.4 The potentiometric measurement uses a cyanide ion selective electrode and double junction reference electrode to quantitate the cyanide ion. It is essential that both the sample and the standard to have comparable ionic strengths.

3. Definitions

3.1 Simple cyanides in this method are defined as cyanide ion and easily dissociated complex cyanide converted to hydrocyanic acid by reaction in a reflux system of an acetate buffer in the presence of lead and zinc ion.

4. Sample handling and preservation

4.1 The sample should be collected in plastic or glass bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and rinsed to remove soluble material.

4.2 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Add an additional 0.6 g ascorbic acid for each liter of sample volume.

4.3 Sulfides slowly convert the cyanide in the sample to thiocyanate. The reaction rate is greatly increased at high pH. Sulfide therefore interferes and should be removed as soon as the sample is collected and before adjustment of the pH. When sulfides are present in the sample, it may be assumed that oxidizing agents are absent. Test for the presence of sulfide by placing a drop of the sample on a strip of lead acetate test paper that has been previously moistened with the acetic acid solution. Darkening of the test paper indicates the presence of sulfide.

4.3.1 Sulfide is removed by treating the sample with small increments of powdered lead carbonate ($PbCO_3$), cadmium carbonate ($CdCO_3$), or with the dropwise addition of lead nitrate [$Pb(NO_3)_2$] solution. When significant quantities of sulfide must be removed, the addition of $PbCO_3$ or $CdCO_3$ is preferred. $Pb(NO_3)_2$ may unduly depress the pH and with $Pb(OAc)_2$ additions, the acetic acid that will distill over may neutralize too much NaOH in the absorber. Black PbS precipitates in samples containing sulfide. Repeat the operation until no more lead sulfide forms, as indicated by testing the supernatant liquid with $Pb(AOc)_2$ test paper. It is not necessary to filter the liquid, since sulfide will not distill over into the scrubber during distillation. This avoids the removal of insoluble cyanides.

4.4 Samples must be preserved with 2 mL of 10N sodium hydroxide per liter of sample (pH 12) at the time of sample collection. (Additional base may be necessary to ensure that the sample pH $\geq$ 12).

4.5 Samples should be analyzed as soon as possible. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain the temperature at 4°C.

4.6 Minimize exposure of the samples to ultraviolet radiation. Photodecomposition of the iron cyanides may significantly increase the cyanide content of the sample. (Remove interferences in the hood under incandescent light conditions.)

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in Sections 8.1 through 8.5.

5.2 Fatty acids, which distill and form soaps in the alkaline scrubber solution, make quantitation by titrimetric or colorimetric means difficult. (This is not a problem if the ion-selective electrode is used.) The fatty acids should be removed by extraction before distillation. (Caution: This operation should be performed in a fume hood and the sample left there until it can be made basic again after extraction.) Acidify the sample with acetic acid (1 + 9) to pH 6-7. Extract with iso-octane, hexane, or chloroform (preference in order named) with a solvent volume equal to 20% of the sample volume. One extraction usually is adequate to eliminate the interference. Avoid multiple extractions or a long contact time at low pH to minimize the loss of HCN. When the extraction is completed, immediately raise the pH to ≥12 with NaOH solution.

5.3 Organic thiocyanates will distill over and form turbid solutions that adversely affect quantitation by titrimetric or colorimetric and electrochemical means. These compounds may be minimized by the extraction procedure outlined for removal of fatty acids.

5.4 Aldehydes react with cyanide to form nitriles, which are further hydrolyzed to their corresponding acids and ammonia under the distillation conditions. Some of the aldehydes may be removed by the extraction procedure outlined in Section 5.2.

5.5 Other possible interferences include substances that might contribute color or turbidity. In most cases, the distillation procedure will remove these.

6. Apparatus

6.1 The reflux distillation apparatus is shown in Figure 1.* The boiling flask should be of 1-liter size with an inlet tube and provision for a condenser.

6.2 Microburet, 5.0 mL (for titration).

6.3 Spectrophotometer suitable for measurement at 578 nm or 620 nm with a 1.0 cm cell or larger.

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*Figure 1 is given at the end of the Appendix.

6.4 A cyanide ion selective electrode, a double junction reference electrode, an expanded scale mV meter or specific ion meter, and a magnetic stirrer with TFE fluorocarbon-coated stirring bar.

7. Reagents

7.1 Sodium hydroxide solution, 1.25 N: Dissolve 50 g NaOH in distilled water and dilute to 1 liter with distilled water.

7.2 Cadmium carbonate: Powdered.

7.3 Ascorbic acid: Crystals.

7.4 Dilute sodium hydroxide solution, 0.25 N: Dilute 200 mL of sodium hydroxide solution (7.1) to 1 liter with distilled water.

7.5 Zinc and lead acetate solution: Dissolve 50 g zinc acetate $Zn(C_2H_3O_2)\cdot 2H_2O$ and 86.4 g lead acetate $Pb(C_2H_3O_2)_2\cdot 3H_2O$ in 500 mL water and dilute to 1 liter.

7.6 Acetate buffer solution: Dissolve 410 g of sodium acetate trihydrate ($NaC_2H_3O_2\cdot 3H_2O$) in 500 mL of water. Add glacial acetic acid to pH 4.5, approximately 500mL .

7.7 Stock cyanide solution, 1 mg/mL : Dissolve 2.51 g KCN and 2 g KOH in 1 liter of distilled water. Standardize with 0.0192 N $AgNO_3$. Dilute to appropriate concentration so that 1mL = 1 mg CN^-.

7.8 Standard cyanide solution, intermediate 50 mg/L: Dilute 50 mL of stock solution (7.7) to 1 liter with distilled water.

7.9 Standard cyanide solution. 5 mg/L: Prepare fresh daily by diluting 100.0 mL of intermediate solution (7.8) to 1 liter with distilled water and store in a glass-stoppered bottle.

7.10 Standard silver nitrate solution: Prepare by crushing approximately 5 g of $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g dried $AgNO_3$, dissolve in distilled water, and dilute to 1 liter (1 mL = 1 mg CN^-).

7.11 Rhodanine indicator: Dissolve 20 mg p-dimethylaminobenzalrhodanine in 100mL of acetone.

7.12 Chloramine-T solution: Dissolve 1 g of white, water-soluble chloramine-T in 100 mL of distilled water and refrigerate until ready to use. Prepare fresh weekly.

7.13 Color reagent - One of the following may be used:

7.13.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250-mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid.

Add 75 mL of pyridine and mix. Add 15 mL of HCl (sp gr 1.19); mix and cool to room temperature. Dilute to 250 ml with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.13.2 Pyridine-pyrazolone solution:

7.13.2.1 3-methyl-1-phenyl-2-pyrazolin-5-one, reagent saturated solution: Add 0.25 g of this compound to 50 mL distilled water, head to 60° C with stirring. Cool to room temperature.

7.13.2.2 3,3'-dimethyl-1,1'-diphenyl-(4,4'-bi-2-pyrazoline)-5,5'-dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 mL pyridine.

7.13.2.3 Pour solution (7.13.2.1) through non-acid-washed filter paper and collect the filtrate. Through the same filter pour solution (7.13.2.2) collecting the filtrate in the same container as the filtrate from (7.13.2.1). Mix until the filtrates are homogeneous. The mixed reagent reacts with cyanide to give a pink color.

7.14 Methyl red indicator: Prepare 0.02 g dissolved in 60 mL water and 40 mL acetic acid.

7.15 Boiling chips.

8. Procedure

8.1 Place 500 mL of sample, or an aliquot diluted to 500 mL, in the 1-liter boiling flask. Add 50 mL of sodium hydroxide (7.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the vacuum train.

8.2 Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube. CAUTION: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.3 Add 2-3 drops of the methyl red indicator to the reaction flask.

8.4 Add 10 mL each of the acetate buffer (7.6) and zinc-lead acetate solutions (7.5) through the air inlet tube.

8.5 Rinse the air inlet tube with a few ml of water and allow the air flow to mix the contents of the flask. (If the solution is not pink, add acetic acid dropwise through the air inlet tube until there is a permanent color change).

8.6 After adding boiling chips to the flask and with the condenser cooling water on, heat the solution to boiling, taking care to prevent the solution from backing into the air inlet tube. (Ensure that the solution remains pink during the distillation. The dropwise addition of more acid or indicator may be necessary).

8.7 Reflux for 1 hour

8.8 Turn off the heat, but maintain the air flow for at least an additional 15 minutes.

8.9 Quantitatively transfer the solution from the absorber into a 100-mL volumetric flask.

8.10 Analyze this solution, or an aliquot of this solution, for cyanide using the titrimetric, colorimetric, or potentiometric methods of analysis.

8.11 Titrimetric method of analysis.

8.11.1 If the sample contains more than 1 mg of CN^-, transfer the distillate, or a suitable aliquot diluted to 100 mL to a 500-mL Erlenmeyer flask. Add 10-12 drops of the rhodanine indicator (7.11).

8.11.2 Titrate with standard silver nitrate (7.10) to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.11.3 The analyst should familiarize himself (herself) with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5- or 10-mL microburet may be conveniently used to obtain a more precise titration.

8.12 Colorimetric method of analysis

8.12.1 Withdraw 20 mL or less of the solution from the flask and transfer to a 100- mL volumetric flask. If less than 20 mL is taken, dilute to 20 mL with 0.25 N sodium hydroxide solution (7.4). Add 6 mL of sodium phosphate solution (7.6) and mix.

8.12.1.1 Pyridine-barbituric acid method: Add 2 mL of chloramine-T (7.12) and mix. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (7.13.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development, then read absorbance at 578 nm in a 1-cm cell within 15 minutes.

8.12.1.2 Pyridine-pyrazolone method: Add 0.5 mL chloramine-T (7.12) and mix. After 1 to 2 minutes, add 5 mL of pyridine-pyrazolone solution (7.13.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes read the absorbance at 620 nm in a 1-cm cell. NOTE: More than 0.5 mL chloramine-T will prevent the color from developing with pyridine-pyrazolone.

8.12.2 Prepare a series of standards by pipeting suitable volumes of standard solution into 100-mL volumetric flasks. To each standard add 50 mL of 1.25 N sodium hydroxide and dilute to 100 mL with distilled water. Prepare as follows:

mL of Standard Solution (5 µg/mL CN^-)	Concentration CN^- (mg CN^-/100mL)
1	0.005
2.0	0.010
5.0	0.025
10.0	0.050
15.0	0.075
20.0	0.100

8.12.2.1 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentration.

8.12.2.2 It is not necessary that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared with similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within ± 10% of the undistilled standards, the operator should find the cause of the apparent error before proceeding.

8.12.3 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to ensure a level of 20 µg/L or a significant increase in absorbance value. Proceed with the analysis as in Section 8.1, using the same flask and system from which the previous sample was just distilled.

8.13 Potentiometric method of analysis.

8.13.1 Prepare a series of standards by pipeting suitable volumes of a standard solution into 100-mL volumetric flasks. To each standard add 50 mL of 1.25 N NaOH and dilute to 100 mL with distilled water. Prepare as follows:

mL of Standard Solution	Concentration CN ($mg\ CN^-/100\ mL$)
($0.5\ \mu g/mL\ CN^-$)	
2.0	0.0010
5.0	0.0025
10.0	0.005
($5\ \mu g/mL\ CN^-$)	
2.0	0.010
5.0	0.025
10.0	0.050
($50\ \mu g/mL\ CN^-$)	
2.0	0.100
5.0	0.250
10.0	0.50

8.13.1.1 Transfer the standard solutions into 150-mL beakers prerinsed with a small portion of the standard being tested. Immerse the cyanide and double junction reference electrodes in the solution and mix on a magentic stirrer. Maintain as closely as possible the same stirring rate and temperature for all solutions.

8.13.1.2 After equilibrium is reached (at least 5 minutes and not more than 10 minutes) record the millivolt reading and plot the CN^- concentrations versus millivolt reading on similogarithmic graph paper. A straight line with a slope of 59 mV indicates that the instrument is operating properly.

8.13.1.3 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared with similar values on the curve to ensure that the distillation technique is reliable. If the distilled standards do not agree within ±10% of the undistilled standards, the operator should find the cause of the apparent error before proceeding.

8.13.2 Place the absorption liquid into a 150-mL beaker and proceed with the analysis as in Section 8.11.1. Determine the CN^- concentration by observing the millivolt reading and referring to the calibration curve established in Section 8.11.1. The method of known addition can be used for measuring occasional samples, since the preparation of a calibration curve is not required.

8.13.3 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to ensure a level of 20 µg/L or a significant increase in values. Proceed with the analysis as in Section 8.1, using the same flask and system from which the previous sample was just distilled.

9. Calculation

9.1 Using the titrimetric procedure, calculate the concentration of CN^- as follows:

$$CN^- \text{ (mg/L)} = \frac{(A-B)(1000)(100\text{ mL})}{(\text{mL of original sample})(\text{mL of aliquot titrated})}$$

where:

A = Volume of $AgNO_3$ used for titration of sample
A = Volume of $AgNO_3$ used for titration of blank.

9.2 Using the colorimetric procedure, calculate the concentration of CN^- as follows:

$$CN^- \text{ (µg/L)} = \frac{(A)(1000)(100)}{(B)(C)}$$

where:

A = µg CN^- read from standard curve
B = mL of original sample taken for distillation
C = mL of scrubber solution taken for colorimetric analysis.

9.3 Using the potentiometric procedure, calculate the concentration of CN^- as follows:

$$CN^- \text{ (µg/L)} = \frac{(A)(1000)(100)}{(B)}$$

where:

A = µg CN^- read from standard curve
B = mL of original sample taken for distillation

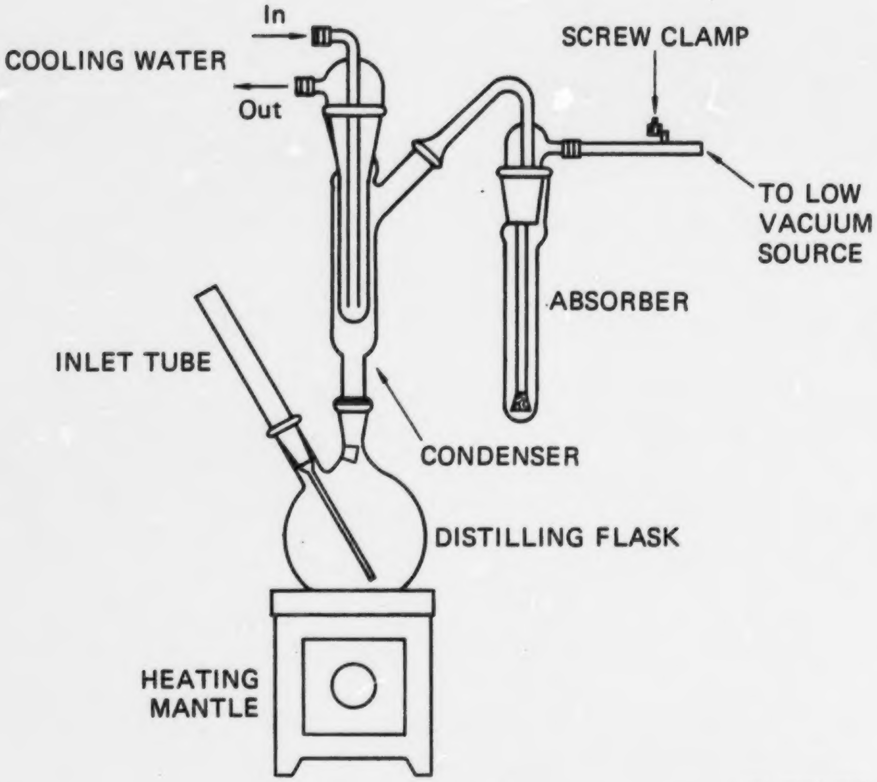
In
COOLING WATER
Out
SCREW CLAMP
TO LOW VACUUM SOURCE
ABSORBER
INLET TUBE
CONDENSER
DISTILLING FLASK
HEATING MANTLE
SA-7854-23R

FIGURE 1 CYANIDE DISTILLATION APPARATUS

Appendix C

EPA PROCEDURE FOR ANALYSIS OF CYANIDES AMENABLE TO CHLORINATION

1. Scope and Application

1.1 This method is applicable to the determination of cyanides in drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/L (0.1 mg/100 mL of absorbing liquid).

1.3 The colorimetric procedure is used for concentrations below 1 mg/mL and is sensitive to about 0.02 mg/L.

1.4 The potentiometric procedure is used for concentrations between 26 and 0.02 mg/L. The lower limit can be extended through the use of a calibration curve to 0.002 mg/L. Higher concentrations can be measured, but since these increase erosion of the membrane, measurements above 26 mg/L cyanide should be done only occasionally.

2. Summary of method

2.1 A portion of the sample is chlorinated to decompose the cyanide amenable to chlorination. Subsequently, total cyanide is determined in both the chlorinated and original sample. The difference between the total cyanide concentration found in the two parts is expressed as "cyanides amenable to chlorination."

2.1.1 Cyanide as hydrocyanic acid (HCN) is released from cyanide compounds by means of a reflux distillation and absorbed in a sodium hydroxide solution. The cyanide in the absorbing solution is determined volumetrically, colorimetrically, or electrometrically.

2.2 The volumetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver-sensitive indicator.

2.3 In the colorimetric measurement the cyanide is converted to cyanogen chloride (CNCl) by reaction with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on the addition of a pyridine-pyrazalone or a pyridine-barbituric acid reagent. The absorbance of the resulting colored solution is read at 620 nm when using pyridine-pyrazalone and 578 nm when using the pyridine-barbituric acid reagent. It is essential that both the sample and the standards have comparable ionic strengths.

2.4 The potentiometric measurement uses a cyanide ion selective electrode and double junction reference electrode to quantitate the cyanide ion. It is essential that both the sample and the standard have comparable ionic strengths.

3. Definitions

3.1 Cyanide is defined as cyanide ion and complex cyanide converted to hydrocyanic acid by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

4. Sample handling and preservation

4.1 The sample should be collected in plastic or glass bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and rinsed to remove soluble material.

4.2 Oxidizing agents such as chlorine decompose most to the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Add an additional 0.6 g ascorbic acid for each liter of sample volume. (Large excesses of ascorbic acid may adversely affect the analysis by production of a yellow color in the scrubber solution.)

4.3 Sulfides slowly convert the cyanide in the sample to thiocyanate. The reaction rate is greatly increased at high pH. Sulfide therefore interferes and should be removed as soon as the sample is collected and before adjustment of the pH. When sulfides are present in the sample, it may be assumed that oxidizing agents are absent. Test for the presence of sulfide by placing a drop of the sample on a strip of lead acetate test paper that has been previously moistened with the acetic acid solution. Darkening of the test paper indicates the presence of sulfide.

4.3.1 Sulfide is removed by treating the sample with small increments of powdered lead carbonate ($PbCO_3$), cadmium carbonate ($CdCO_3$), or with the dropwise addition of lead nitrate [$Pb(NO_3)_2$] solution. (When significant quantities of sulfide must be removed, the addition of $PbCO_3$, or $CdCO_3$ is preferred. $Pb(NO_3)_2$ may unduly depress the pH and with $Pb(OAc)_2$ additions, the acetic acid--which will distill over--may neutralize too much NaOH in the absorber). Black PbS precipitates in samples containing sulfide. Repeat the operation until no more lead sulfide forms, as indicated by testing the supernatant liquid with $Pb(OAc)_2$ test paper. Immediately filter through dry paper into a dry beaker and stabilize the sample by adjusting the pH. (Insoluble cyanides may be removed from the sample by this procedure.)

4.4 Samples must be preserved with 2 mL of 10N sodium hydroxide per liter of sample (pH 12) at the time of sample collection. (The addition of more base may be required to ensure that the pH of the sample is ≥ 12.)

4.5 Samples should be analyzed as soon as possible. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain the temperature at 4°C.

4.6 Minimize the exposure of the samples to ultraviolet radiation. Photodecomposition of the iron cyanides may significantly increase the cyanide content of the sample. (Remove interferences in the hood under incandescent light conditions, etc.)

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in Sections 8.1 through 8.5.

5.2 Fatty acids, which distill and form soaps in the alkaline scrubber solution, make quantitation by titrimetric or colorimetric means difficult. (This is not a problem if the ion-selective electrode is used) The fatty acids should be removed by extraction before distillation. (Caution: This operation should be performed in a fume hood and the sample left there until it can be made basic again after extraction.) Acidify the sample with acetic acid (1 + 9) to pH 6-7. Extract with iso-octane, hexane, or chloroform (preference in order named) with a solvent volume equal to 20% of the sample volume. One extraction usually is adequate to eliminate the interference. Avoid multiple extractions or a long contact time at low pH to minimize the loss of HCN. When the extraction is completed, immediately raise the pH to ≥ 12 with NaOH solution.

5.3 Organic thiocyanates will distill over and form turbid solutions that adversely affect quantitation by titrimetric or colorimetric means. These compounds also adversely affect quantitation by electrochemical means. These compounds may be minimized by the extraction procedure outlined for removal of fatty acids.

5.4 Aldehydes react with cyanide to form nitriles, which are further hydrolyzed to their corresponding acids and ammonia under the distillation conditions. Some of the aldehydes may be removed by the extraction procedure outlined in Section 5.2.

5.5 Thiocyanates are decomposed during distillation to sulfide, which interferes with quantitation of cyanide. The procedure outlined in Section 4.3 can be used to remove sulfide from the scrubber solution.

6. Apparatus

6.1 The reflux distillation apparatus is shown in Figure 1.* The boiling flask should be of 1-liter size with an inlet tube and provision for a condenser.

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*Figure 1 is given at the end of the Appendix.

6.2 Microburet, 5.0 mL (for titration).

6.3 Spectrophotometer suitable for measurement at 578 nm or 620 nm with a 1.0 cm cell or larger.

6.4 A cyanide ion selective electrode, a double junction reference electrode, an expanded scale mV meter or specific ion meter and a magnetic stirrer with TFE fluorocarbon-coated stirring bar.

7. Reagents

7.1 Sodium hydroxide solution, 1.25 N: Dissolve 50 g NaOH in distilled water and dilute to 1 liter with distilled water.

7.2 Cadmium carbonate: Powdered.

7.3 Ascorbic acid: Crystals.

7.4 Dilute sodium hydroxide solution, 0.25 N: Dilute 200 mL of sodium hydroxide solution (7.1) to 1 liter with distilled water.

7.5 Sulfuric acid: Concentrated.

7.6 Sodium dihydrogenphosphate, 1M: Dissolve 138 g $NaH_2PO_4.H_2O$ in 1 liter of distilled water. Refrigerate this solution.

7.7 Stock cyanide solution, 1 mg/mL: Dissolve 2.51 g KCN and 2 g KOH in 1 liter distilled water. Standardize with 0.0192N $AgNO_3$. Dilute to appropriate concentration so that 1 mL = 1 mg CN .

7.8 Standard cyanide solution, intermediate: 50 mg/L: Dilute 50.0 mL of stock solution (7.7) to 1 liter with distilled water.

7.9 Standard cyanide solution, 5 mg/L: Prepare fresh daily by diluting 100.0 mL of intermediate solution (7.8) to 1 liter with distilled water and store in a glass-stoppered bottle.

7.10 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g dried $AgNO_3$, dissolve in distilled water, and dilute to 1 liter (1 mL = 1 mg CN^-).

7.11 Rhodanine indicator: Dissolve 20 mg p-dimethylaminobenzalrhodanine in 100 mL of acetone.

7.12 Chloramine-T solution: Dissolve 1 g of white, water-soluble chloramine-T in 100 mL of distilled water and refrigerator until ready to use. Prepare fresh weekly.

7.13 Color reagent - One of the following may be used:

7.13.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250-mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of HCl (sp gr 1.19); mix and cool to room temperature. Dilute to 250 mL with distilled water and mix. This reagent is stable for approximately six months if stored in a cool dark place.

7.13.2 Pyridine-pyrazolone solution:

7.13.2.1 3-methyl-1-phenyl-2-pyrazolin-5-in-one, reagent saturated solution: Add 0.25 g of this compound to 50 mL distilled water, heat to 60°C with stirring. Cool to room temperature.

7.13.2.2 3,3'-dimethyl-1,1'-diphenyl-(4,4'-bi-2-pyrazoline)-5,5'-dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 mL pyridine.

7.13.2.3 Pour solution (7.13.2.1) through non-acid-washed filter paper. Collect the filtrate. Pour solution through the same filter (7.13.2.2), collecting the filtrate in the same container as the filtrate from (7.13.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color, but this does not affect the color production with cyanide if used within 24 hours of preparation.

7.14 Magnesium chloride solution: Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1-liter flask; dissolve and dilute to 1 liter with distilled water.

7.15 Calcium hypochlorite solution: Dissolve 5 g calcium hypochlorite $[Ca(OCl)_2]$ in 100 mL distilled water.

7.16 Boiling chips.

8. Procedure

8.1 Two sample aliquots are required to determine cyanides amenable to chlorination. To one 500-mL aliquot or a volume diluted to 500 mL, add calcium hypochlorite (7.15) dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide (7.1).

8.2 Test for residual chlorine with KI-starch test paper and maintain this excess for 1 hour, continuing agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional hypochlorite solution.

8.3 After 1 hour, add 0.5 g ascorbic acid (7.3) until KI-starch test paper shows no residual chlorine. Add an additional 0.5 g of ascorbic acid to ensure the presence of excess reducing agent. (large excesses of ascorbic acid may adversely affect analysis)

8.4 Test for total cyanide in both the chlorinated and unchlorinated aliquots by the procedure outlined in the following sections.

8.5 Place 500 mL of sample, or an aliquot diluted to 500 mL, in the 1-liter boiling flask. Add 50 mL of sodium hydroxide (7.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the vacuum train.

8.6 Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.
CAUTION: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the flow rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.7 Slowly add 25 mL concentrated sulfuric acid (7.5) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride solution (7.14) into the air inlet tube and wash down with a stream of water. Add few boiling chips through the air inlet tube and wash down with distilled water.

8.8 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off the heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect the absorber and close off the vacuum source.

8.9 Quantitatively transfer the solution from the absorber into a 100-mL volumetric flask.

8.10 Analyze this solution, or an aliquot of this solution, for cyanide using the titrimetric, colorimetric, or potentiometric method of analysis.

8.11 Titrimetric method of analysis

8.11.1 If the sample contains more than 1 mg of CN^-, transfer the distillate, or a suitable aliquot diluted to 100 mL to a 500-mL Erlenmeyer flask. Add 10-12 drops of the rhodanine indicator (7.11).

8.11.2 Titrate with standard silver nitrate (7.10) to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.11.3 The analyst should familiarize himself (herself) with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5- or 10-mL microburet may be conveniently used to obtain a more precise titration.

8.12 Colorimetric method of analysis

8.12.1 Withdraw 20 mL or less of the solution from the flask and transfer to a 100-mL volumetric flask. If less than 20 mL is taken, dilute to 20 mL with 0.25 N sodium hydroxide solution (7.4). Add 6 mL of sodium phosphate solution (7.6) and mix.

8.12.1.1 Pyridine-barbituric acid method: Add 2 mL of chloramine-T (7.12) and mix. After 1 to 2 minutes, add 4 ml of pyridine-barbituric acid solution (7.13.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development, then read absorbance at 578 nm in a 1-cm cell within 15 minutes.

8.12.1.2 Pyridine-pyrazolone method: Add 0.5 mL chloramine-T (7.12) and mix. After 1 to 2 minutes, add 5 mL of pyridine-pyrazolone solution (7.13.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes read the absorbance at 620 nm in a 1-cm cell. NOTE: More than 0.5 mL chloramine-T will prevent the color from developing with pyridine-pyrazolone.

8.12.2 Prepare a series of standards by pipeting suitable volumes of standard solution into 100-mL volumetric flasks. To each standard add 50 mL of 1.25 N sodium hydroxide and dilute to 100 mL with distilled water. Prepare as follows:

mL of Standard Solution (5 µg/mL CN^-)	Concentration CN^- (mg CN^-/100 mL)
1	0.005
2.0	0.010
5.0	0.025
10.0	0.050
15.0	0.075
20.0	0.100

8.12.2.1 Prepare a standard curve by plotting absorbance. of standard versus cyanide concentration.

8.12.2.2 It is not necessary that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within ±10% of the undistilled standards, the operator should find the cause of the apparent error before proceeding.

8.12.3 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to ensure a level of 20 µg/L or a significant increase in absorbance value. Proceed with the analysis as in Section 8.1, using the same flask and system from which the previous sample was just distilled.

8.13 Potentiometric method of analysis.

8.13.1 Prepare a series of standards by pipeting suitable volumes of a standard solution into 100-mL volumetric flasks. To each standard add 50 mL of 1.25 N NaOH and dilute to 100 mL with distilled water. Prepare as follows:

mL of Standard Solution	Concentration CN (mg CN^-/100 mL)
(0.5 µg/mL CN^-)	
2.0	0.0010
5.0	0.0025
10.0	0.005
(5 µg/mL CN^-)	
2.0	0.010
5.0	0.025
10.0	0.050
(50 µg/mL CN^-)	
2.0	0.100
5.0	0.250
10.0	0.50

8.13.1.1 Transfer the standard solutions into 150-mL beakers prerinsed with a small portion of the standard being tested. Immerse the cyanide and double junction reference electrodes in the solution and mix well on a magnetic stirrer. Maintain as closely as possible the same stirring rate and temperature for all solutions.

8.13.1.2 After equilbrium is reached (at least 5 minutes and not less than 10 minutes), record the millivolt reading and plot the CN^- concentrations versus millivolt reading on semilogarithmic graph paper. A straight line with a slope of 59 mV indicates that the instrument is operating properly.

8.13.1.3 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If the distilled standards do not agree within ±10% of the undistilled standards, the operator should find the cause of the apparent error before proceeding.

8.13.2 Place the absorption liquid into a 150-mL beaker and proceed with the analysis as in Section 8.13.1. Determine the CN^- concentration by observing the millivolt reading and referring to the calibration curve established in Section 8.13.1. The method of known addition can be used for measuring occasional samples since the preparation of a calibration curve is not required.

8.13.3 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to ensure a level of 20 µg/L or a significant increase in values. Proceed with the analysis as in Section 8.1 using the same flask and system from which the previous sample was just distilled.

9. Calculations

9.1 Using the titrimetric procedure, calculate the concentration of CN^- as follows:

$$CN^-\ (\text{mg/L}) = \frac{(A-B)(1000)(100\text{mL})}{(\text{mL of original sample})(\text{mL of aliquot titrated})}$$

where:

A = Volume of $AgNO_3$ used for titration of sample
B = Volume of $AgNO_3$ used for titration of blank.

9.2 Using the colorimetric procedure, calculate the concentration of CN^- as follows:

$$CN^-\ (\mu\text{g/L}) = \frac{(A)(100)(100)}{(B)(C)}$$

where:

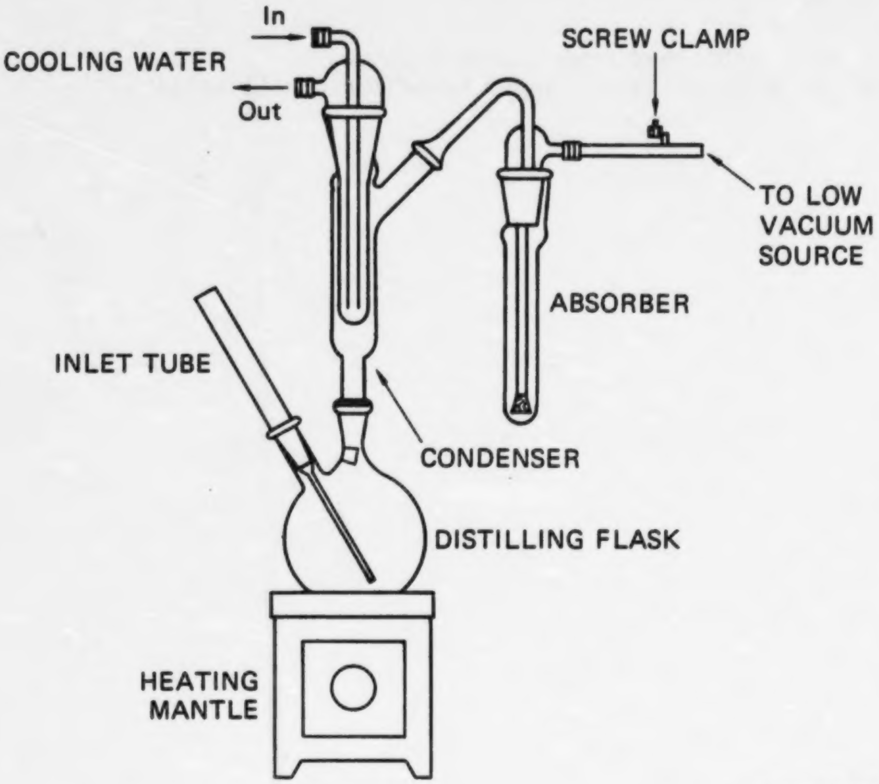
A = µg CN^- read from standard curve
B = mL of original sample taken for distillation
C = mL of scrubber solution taken for colorimetric analysis.

9.3 Using the potentiometric procedure, calculate the concentration of CN^- as follows:

$$CN^- \ (\mu g/L) = \frac{(A)(1000)(100)}{(B)}$$

where:

A = µg CN^- read from standard curve
B = mL of original sample taken for distillation



In
COOLING WATER
Out
SCREW CLAMP
TO LOW VACUUM SOURCE
ABSORBER
INLET TUBE
CONDENSER
DISTILLING FLASK
HEATING MANTLE

SA-7854-23R

FIGURE 1 CYANIDE DISTILLATION APPARATUS

Appendix D

LIGAND-EXCHANGE METHOD OF ANALYSIS FOR TOTAL CYANIDE

1. Scope and application

1.1 This method is applicable to the determination of cyanides in drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodaine indicator is used for measuring concentrations of cyanide exceeding 1 mg/L (0.1 mg/100 mL of absorbing liquid).

1.3 The colorimetric procedure is used for concentrations below 1 mg/ mL and is sensitive to about 0.02 mg/L.

1.4 The potentiometric procedure is used for concentrations between 26 and 0.02 mg/L. The lower limit can be extended through the use of a calibration curve to 0.002 mg/L. Higher concentrations can be measured but since these increase erosion of the membrane, measurements above 26 mg/L cyanide should be made only occasionally.

2. Summary of method

2.1 The cyanide is released from cyanide complexes by means of a ligand exchange reaction during a reflux distillation. The cyanide, as hydrocyanic acid (HCN), is aerated from the sample and absorbed in a sodium hydroxide scrubber solution. The cyanide in the absorbing solution is then quantitated by volumetric titration, colorimetry, or potentiometry.

2.2 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver-sensitive indicator.

2.3 In the colorimetric procedure the cyanide is converted to cyanogen chloride (CNCl) by reaction with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on the addition of a pryidine-pyrazalone or a pyridine-barbituric acid reagent. The absorbance of the resulting colored solution is read at 620 nm when using pyridine-pyrazalone and 578 nm when using the pyridine-barbituric acid reagent. It is essential that both the sample and the standards be of comparable ionic strength.

2.4 The potentiometric measurement uses a cyanide ion selective electrode and double junction reference electrode to quantitate the cyanide ion. It is essential that both the sample and the standard have comparable ionic strengths.

3. Definitions

3.1 Cyanide is defined as free cyanide ion and cyanide from metal complexes that is converted to hydrocyanic acid by reaction in this system.

4. Sampling handling and preservation

4.1 The sample should be collected in plastic or glass bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and rinsed to remove soluble material.

4.2 Oxidizing agents such as chlorine decompose most to the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Add an additional 0.6 g ascorbic acid for each liter of sample volume.

4.3 Sulfides slowly convert the cyanide in the sample to thiocyanate. The reaction rate is greatly increased at high pH. Sulfide therefore interferes and should be removed as soon as the sample is collected and before adjustment of the pH. When sulfides are present in the sample, it may be assumed that oxidizing agents are absent. Test for the presence of sulfide by placing a drop of the sample on a strip of lead acetate test paper that has been previously moistened with the acetic acid solution. Darkening of the test paper indicates the presence of sulfide.

4.3.1 Sulfide is removed by treating the sample with small increments of powdered lead carbonate ($PbCO_3$), cadmium carbonate ($CdCO_3$), or with the dropwise addition of lead nitrate [$Pb(NO_3)_2$] solution. (When significant quantities of sulfide must be removed, the addition of $PbCO_3$, or $CdCO_3$ is preferred. $Pb(NO_3)_2$ may unduly depress the pH and with $Pb(OAc)_2$ additions, the acetic acid that will distill over may neutralize too much NaOH in the absorber.) Black PbS precipitates in samples containing sulfide. Repeat the operation until no more lead sulfide forms, as indicated by testing the supernatant liquid with $Pb(OAc)_2$ test paper. It is not necessary to filter this liquid since $S^=$, as PbS, will not interfere.

4.4 Samples must be preserved with 2 mL of 10N sodium hydroxide per liter of sample (pH 12) at the time of sample collection. (It may be necessary to add additional base to ensure that the pH of the sample is ≥12.)

4.5 Samples should be analyzed as soon as possible. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain the temperature at 4°C.

4.6 Minimize exposure of the samples to ultraviolet radiation. Photodecomposition of the iron cyanides may significantly increase the cyanide content of the sample. (Remove interferences in the hood under incandescent light, etc.)

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in Sections 8.1 through 8.5.

5.2 Fatty acids, which distill and form soaps in the alkaline scrubber solution, make quantitation by titrimetric or colorimetric means difficult. (This problem is not encountered if the ion selective electrode is used.) The fatty acids should be removed by extraction before distillation. (Caution: This operation should be performed in a fume hood and the sample left there until it can be made basic again after extraction.) Acidify the sample with acetic acid (1 + 9) to pH 6-7. Extract with iso-octane, hexane, or chloroform (preference in order named) with a solvent volume equal to 20% of the sample volume. One extraction usually is adequate to reduce the fatty acid concentration below the interference. Avoid multiple extractions or a long contact time at low pH to minimize the loss of HCN. When the extraction is completed, immediately raise the pH to ≥12 with NaOH solution.

5.3 Organic thiocyanates will distill over and form turbid solutions that adversely affect quantitation by titrimetric or colorimetric finishes. These compounds also adversely affect quantitation by electrochemical means. These compounds may be minimized by the extraction procedure outlined for removal of fatty acids.

5.4 Aldehydes may react with the cyanide to produce nitriles, which are further hydrolyzed to the corresponding acids and ammonia. Some of the aldehydes may be removed by the extraction procedure outlined in Section 5.2.

5.5 Other possible interferences include substances that might contribute color or turbidity. In most cases, the distillation procedure will remove these.

6. Apparatus

6.1 The reflux distillation apparatus is shown in Figure 1.* The boiling flask should be of 1-liter size with an inlet tube and provision for a condenser.

6.2 Microburet, 5.0 mL (for titration).

6.3 Spectrophotometer suitable for measurement at 578 nm or 620 nm with a 1.0 cm cell or larger.

6.4 A cyanide ion selective electrode, a double junction reference electrode, an expanded scale mV meter or specific ion meter, and a magnetic stirrer with TFE fluorocarbon-coated stirring bar.

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*Figure 1 is given at the end of the Appendix.

7. Reagents

7.1 Sodium hydroxide solution, 1.25 N: Dissolve 50 g NaOH is distilled water and dilute to 1 liter with distilled water.

7.2 Cadmium carbonate: Powdered.

7.3 Ascorbic acid: Crystals.

7.4 Dilute sodium hydroxide solution, 0.25 N: Dilute 200 mL of sodium hydroxide solution (7.1) to 1 liter with distilled water.

7.5 Methyl red: Dissolve 0.2 g in 60 mL water and 50 mL glacial acetic acid.

7.6 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g $NaH_2PO_4 \cdot H_2O$ in 1 liter of distilled water. Refrigerate this solution.

7.7 Stock cyanide solution, 1 mg/mL: Dissolve 2.51 g KCN and 2 g KOH in 1 liter distilled water. Standardize with 0.0192N $AgNO_3$. Dilute to appropriate concentration so that 1 mL = 1 mg CN^-.

7.8 Standard cyanide solution, intermediate, 50 mg/L: Dilute 50.0 mL of stock solution (7.7) to 1 liter with distilled water.

7.9 Standard cyanide solution, 5 mg/L; Prepare fresh daily by diluting 100.0mL of intermediate solution (7.8) to 1 liter with distilled water and store in a glass-stoppered bottle.

7.10 Standard silver nitrate solution, 0.0192 N: Prepared by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 50°C. Weigh out 3.2647 g dried $AgNO_3$, dissolve in distilled water, and dilute to 1 liter (1 mL = 1 mg CN^-).

7.11 Rhodanine indicator: Dissolve 20 mg p-dimethylaminobenzalrhodanine in 100 mL of acetone.

7.12 Chloramine-T solution: Dissolve 1 g of white, water-soluble chloramine in 100 mL of distilled water and refrigerate until ready to use. Prepare fresh weekly.

7.13 Color reagent - One of the following may be used:

7.13.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250-mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of HCl (sp gr 1.19); mix and cool to room temperature. Dilute to 250 mL with distilled water and mix. This reagent is stable for approximately six months if stored in a cool dark place.

7.13.2 Pyridine-pyrazolone solution:

7.13.2.1 3-methyl-1-phenyl-2-pyrazolin-5-one reagent saturated solution: Add 0.25 g of this compound to 50 mL distilled water, heat to 60°C with stirring. Cool to room temperature.

7.13.2.2 3,3'-dimethyl-1,1'-diphenyl-(4,4'-bi-2-pyrazoline)-5,5'-dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 mL pyridine.

7.13.2.3 Pour solution (7.13.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter pour solution (7.13.2.2), collecting the filtrate in the same container as the filtrate from (7.13.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

7.14 Acetate buffer solution: Dissolve 410 g of sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) in 500 mL of water. Add glacial acetic acid to pH 4.5 (approximately 500 mL).

7.15 TIRON solution: Dissolve 200 g of 1,2-dihydroxy-3,5-benzenedisulfonic acid, disodium salt monohydrate in 1 liter of water.

7.16 TEP solution: Adjust the pH of 250 g of tetraethylenepentamine to 5 with a HCl solution (3 + 1). Dilute to 1 liter with water.

7.17 Lead acetate solution: Dissolve 90 g lead acetate trihydrate ($Pb[C_2H_3O_2]_2 \cdot 3H_2O$) in 1 liter of water.

7.18 Boiling chips.

8. Procedure

8.1 Place 500 mL of sample, or an aliquot diluted to 500 mL in the 1-liter boiling flask. Add 50 mL of sodium hydroxide (7.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the vacuum train.

8.2 Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube. CAUTION: The bubbler rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.3 Add through the air inlet tube the following reagents in the order presented: 5 mL of the lead acetate solution (7.17); 10 mL of the TIRON solution (7.15); 5 mL of the TEP solution (7.16), and 10 mL of the acetate buffer solution (7.14). After each addition, rinse the tube with water and allow the air flow to mix the flask contents. Add a few boiling chips through the air inlet tube and wash down with water.

8.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one-half hour. Turn off the heat and continue the air flow for at least 15 minutes. After cooling the boiling flask, disconnect the absorber and close off the vacuum source.

8.5 Quantitatively transfer the solution from the absorber into a 100-mL volumetric flask.

8.6 This solution, or an aliquot of this solution, is then analyzed for cyanide using the titrimetric, colorimetric, or potentiometric methods of analysis.

8.7 Titrimetric method of analysis

8.7.1 If the sample contains more than 1 mg of CN^-, transfer the distillate, or a suitable aliquot diluted to 100mL to a 500-mL Erlenmeyer flask. Add 10-12 drops of the rhodanine indicator (7.11).

8.7.2 Titrate with standard silver nitrate (7.10) to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.7.3 The analyst should familiarize himself (herself) with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5- or 10-mL microburet may be conveniently used to obtain a more precise titration.

8.8 Colorimetric method of analysis

8.8.1 Withdraw 20 mL or less of the solution from the flask and transfer to a 100-mL volumetric flask. If less than 20 mL is taken, dilute to 20 mL with 0.25 N sodium hydroxide solution (7.4). Add 6 mL of sodium phosphate solution (7.6) and mix.

8.8.1.1 Pyridine-barbituric acid method: Add 2 mL of chloramine-T (7.12) and mix. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (7.13.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development, and read absorbance at 578 nm in a 1-cm cell within 15 minutes.

8.8.1.2 Pyridine-pyrazolone method: Add 0.5 mL chloramine-T (7.12) and mix. After 1 to 2 minutes, add 5 mL of pyridine-pyrazolone solution (7.13.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes, read the absorbance at 620 nm in a 1-cm cell. NOTE: More than 0.5 mL chloramine-T will prevent the color from developing with pyridine-pyrazolone.

8.8.2 Prepare a series of standards by pipeting suitable volumes of standard solution into 100-mL volumetric flasks. To each standard add 50 mL of 1.25 N sodium hydroxide and dilute to 100 mL with distilled water. Prepare as follows:

mL of Standard Solution (5 µg/mL CN^-)	Concentration CN^- (mg CN^-/100 mL)
1	0.005
2.0	0.010
5.0	0.025
10.0	0.050
15.0	0.075
20.0	0.100

8.8.2.1 Prepare a standard curve by plotting absorbance of standard versus cyanide concentration.

8.8.2.2 It is not necessary that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within ±10% of the undistilled standards, the operator should find the cause of the apparent error before proceeding.

8.8.3 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to ensure a level of 20 µg/L or a significant increase in absorbance value. Proceed with the analysis as in Section 8.1, using the same flask and system from which the previous sample was just distilled.

8.9 Potentiometric method of analysis

8.9.1 Prepare a series of standards by pipeting suitable volumes of a standard solution into 100- mL volumetric flasks. To each standard add 50 mL of 1.25 N NaOH and dilute to 100 mL with distilled water. Prepare as follows:

mL of Standard Solution	Concentration CN (mg CN^-/100 mL)
(0.5 µg/mL CN^-)	
2.0	0.0010
5.0	0.0025
10.0	0.005
(5 µg/mL CN^-)	
2.0	0.010
5.0	0.025
10.0	0.050
(50 µg/mL CN^-)	
2.0	0.100
5.0	0.250
10.0	0.50

8.9.1.1 Transfer the standard solutions into 150-mL beakers prerinsed with a small portion of the standard being tested. Immerse the cyanide and double junction reference electrodes in the solution and mix well on a magnetic stirrer. Maintain as closely as possible the same stirring rate and temperature for all solutions.

8.9.1.2 After equilibrium is reached (at least 5 minutes and not more than 10 minutes), record the millivolt reading and plot the CN^- concentrations versus millivolt reading on semilogarithmic graph paper. A straight line with a slope of 59 mV indicates that the instrument is operating properly.

8.9.1.3 It is not necessary that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared with similar values on the curve to ensure that the distillation technique is reliable. If the distilled standards do not agree within ±10% of the undistilled standards, the operator should find the cause of the apparent error before proceeding.

8.9.2 Place the absorption liquid into a 150-mL beaker and proceed with the analysis as in Section 8.9.1. Determine the CN^- concentration by observing the millivolt reading and referring to the calibration curve established in Section 8.9.1.

The method of known addition can be used for measuring occasional samples since the preparation of a calibration curve is not required.

8.9.3 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to ensure a level of 20 μg/L or a significant increase in values. Proceed with the analysis as in Section 8.1, using the same flask and system from which the previous sample was just distilled.

9. Calculations

9.1 Using the titrimetric procedure, calculate the concentration of CN^- as follows:

$$CN^- \text{ (mg/L)} = \frac{(A-B)(1000)(100)}{(\text{mL of original sample})(\text{mL of aliquot titrated})}$$

where:

A = Volume of $AgNO_3$ for titration of sample
B = Volume of $AgNO_3$ for titration of blank.

9.2 Using the colorimetric procedure, calculate the concentration of CN^- as follows:

$$CN^- \text{ (}\mu\text{g/L)} = \frac{(A)(1000)(100)}{(B)(C)}$$

where:

A = μg CN^- read from standard curve
B = mL of original sample taken for distillation
C = mL of scrubber solution taken for colorimetric analysis.

9.3 Using the potentiometric procedure, calculate the concentration of CN^- as follows:

$$CN^- \text{ (}\mu\text{g/L)} = \frac{(A)(1000)(100)}{(B)}$$

where:

A = μg CN^- read from standard curve
B = mL of original sample taken for distillation

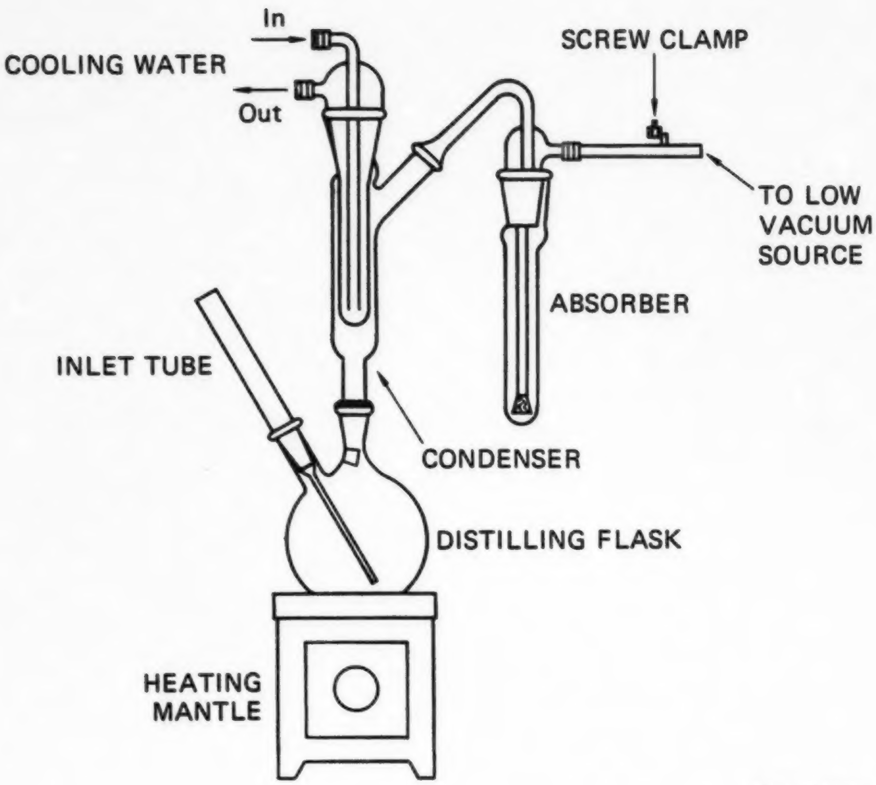
In
COOLING WATER
Out
SCREW CLAMP
TO LOW VACUUM SOURCE
ABSORBER
INLET TUBE
CONDENSER
DISTILLING FLASK
HEATING MANTLE
SA-7854-23R

FIGURE 1 CYANIDE DISTILLATION APPARATUS

Appendix E

EPA PROCEDURE FOR ANALYSIS OF TOTAL CYANIDE

1. Scope and application

1.1 This method is applicable to the determination of cyanides in drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/L (0.1 mg/100 mL of absorbing liquid).

1.3 The colorimetric procedure is used for concentrations below 1 mg/mL and is sensitive to about 0.02 mg/L.

1.4 The potentiometric procedure is used for concentrations between 26 and 0.02 mg/L. The lower limit can be extended through the use of a calibration curve to 0.002 mg/L. Higher concentrations can be measured but since these increase erosion of the membrane, measurements above 26 mg/L cyanide should be done only occasionally.

2. Summary of method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then quantitated by volumetric titration, colorimetry, or potentiometry.

2.2 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver-sensitive indicator.

2.3 In the colorimetric measurement the cyanide is converted to cyanogen chloride (CNCl) by reaction with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on the addition of a pyridine-pyrazalone or a pyridine-barbituric acid reagent. The absorbance of the resulting colored solution is read at 620 nm when using pyridine-pyrazalone and 578 nm when using the pyridine-barbituric acid reagent. It is essential that both the sample and the standards be of comparable ionic strength.

2.4 The potentiometric measurement uses a cyanide ion selective electrode and double junction reference electrode to quantitate the cyanide ion. It is essential that both the sample and the standard have comparable ionic strengths.

3. Definitions

3.1 Cyanide is defined as cyanide ion and complex cyanide converted to hydrocyanic acid by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

4. Sample handling and preservation

4.1 The sample should be collected in plastic or glass bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and rinsed to remove soluble material.

4.2 Oxidizing agents such as chlorine decompose most to the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Add an additional 0.6 g ascorbic acid for each liter of sample volume. (Large excesses of ascorbic acid may produce a yellow-colored scrubber solution that interferes with the colorimetric finish.)

4.3 Sulfides slowly convert the cyanide in the sample to thiocyanate. The reaction rate is greatly increased at high pH. Sulfide therefore interferes and should be removed as soon as the sample is collected and before adjustment of pH. When sulfides are present in the sample, it may be assumed that oxidizing agents are absent. Test for the presence of sulfide by placing a drop of the sample on a strip of lead acetate test paper that has been previously moistened with the acetic acid solution. Darkening of the test paper indicates the presence of sulfide.

4.3.1 Sulfide is removed by treating the sample with small increments of powdered lead carbonate ($PbCO_3$), cadmium carbonate ($CdCO_3$), or with the dropwise addition of lead nitrate [$Pb(NO_3)_2$] solution. (When significant quantities of sulfide must be removed, the addition of $PbCO_3$, or $CdCO_3$ is preferred. $Pb(NO_3)_2$ may unduly depress the pH and with $Pb(OAc)_2$ additions, the acetic acid that will distill over may neutralize too much NaOH in the absorber.) Black PbS precipitates in samples containing sulfide. Repeat the operation until no more lead sulfide forms, as indicated by testing the supernatant liquid with $Pb(OAc)_2$ test paper. Immediately filter through dry paper into a dry beaker and stabilize the sample by adjusting the pH. (This may have the adverse effect of removing insoluble cyanides, thereby resulting in abnormally low results.)

4.4 Samples must be preserved with 2 mL of 10N sodium hydroxide per liter of sample (pH 12) at the time of sample collection. (Additional base may be needed to ensure that the pH of the sample is ≥ 11.)

4.5 Samples should be analyzed as soon as possible. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain the temperature at 4°C.

4.6 Minimize exposure of the samples to ultraviolet radiation. Photodecomposition of the iron cyanides may significantly increase the cyanide content of the sample. (Remove interferences in the hood under incandescent light conditions, etc.)

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in Sections 8.1 through 8.5.

5.2 Fatty acids that distill and form soaps in the alkaline scrubber solution make quantitation by titrimetric or colorimetric means difficult. (This is not a problem if the ion-selective electrode is used.) The fatty acids should be removed by extraction before distillation. (Caution: This operation should be performed in a fume hood and the sample left there until it can be made basic again after extraction.) Acidify the sample with acetic acid (1 + 9) to pH 6-7. Extract with iso-octane, hexane, or chloroform (preference in order named) with a solvent volume equal to 20% of the sample volume. One extraction usually is adequate to reduce the fatty acid concentration below the interference. Avoid multiple extractions or a longer contact time at low pH to minimize the loss of HCN. When the extraction is completed, immediately raise the pH to ≥12 with NaOH solution.

5.3 Organic thiocyanates will distill over and form turbid solutions that adversely affect quantitation by titrimetric or colorimetric finishes. These compounds also adversely affect quantitation by electrochemical means. These compounds may be minimized by the extraction procedure outlined for removal of fatty acids.

5.4 Aldehydes react with cyanide to produce nitriles, which are further hydrolyzed to their corresponding acids and ammonia. Some of the aldehydes may be removed by the extraction procedure outlined in Section 5.2.

5.5 Thiocyanates are decomposed during the distillation to sulfide, which interferes with quantitation. The procedure outlined in Section 4.3 can be used to remove sulfide from the scrubber solution.

5.6 Other possible interferences include substances that might contribute color or turbidity. In most cases, the distillation procedure will remove these.

6. Apparatus

6.1 The reflux distillation apparatus is shown in Figure 1.* The boiling flask should be of 1 liter size with an inlet tube and provision for a condenser.

6.2 Microburet, 5.0 mL (for titration).

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*Figure 1 is given at the end of the Appendix.

6.3 Spectrophotometer suitable for measurement at 578 nm or 620 nm with a 1.0 cm cell or larger.

6.4 A cyanide ion selective electrode, a double junction reference electrode, an expanded scale mV meter or specific ion meter, and a magnetic stirrer with TFE fluorocarbon-coated stirring bar.

7. Reagents

7.1 Sodium hydroxide solution, 1.25 N: Dissolve 50 g NaOH in distilled water and dilute to 1 liter with distilled water.

7.2 Cadmium carbonate: Powdered.

7.3 Ascorbic acid: Crystals.

7.4 Dilute sodium hydroxide solution, 0.25 N: Dilute 200 mL of sodium hydroxide solution (7.1) to 1 liter with distilled water.

7.5 Sulfuric acid: Concentrated.

7.6 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g $NaH_2PO_4 \cdot H_2O$ in 1 liter of distilled water. Refrigerate this solution.

7.7 Stock cyanide solution, 1 mg/mL Dissolve 2.51 g KCN and 2 g KOH in 1 liter distilled water. Standardize with 0.0192 N $AgNO_3$. Dilute to appropriate concentration so that 1mL = 1 mg CN^-.

7.8 Standard cyanide solution, intermediate, 50 mg/L: Dilute 50.0 mL of stock solution (7.7) to 1 liter with distilled water.

7.9 Standard cyanide solution, 5 mg/L: Prepare fresh daily by diluting 100.0 mL of intermediate solution (7.8) to 1 liter with distilled water in a glass-stoppered bottle.

7.10 Standard silver nitrate solution, 0.0192 N: Prepared by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 50°C. Weigh out 3.2647 g dried $AgNO_3$, dissolve in distilled water, and dilute to 1 liter (1mL = 1 mg CN^-).

7.11 Rhodanine indicator: Dissolve 20 mg p-dimethylaminobenzalrhodanine in 100 mL of acetone.

7.12 Chloramine-T solution: Dissolve 1 g of white, water-soluble chloramine-T in 100 mL of distilled water and refrigerate until ready to use. Prepare fresh daily.

7.13 Color reagent - One of the following may be used:

7.13.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250-mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of HCl (sp gr 1.19), mix and cool to room temperature. Dilute to 250 mL with distilled water and mix. This reagent is stable for approximately six months if stored in a cool dark place.

7.13.2 Pyridine-pyrazolone solution

7.13.2.1 3-methyl-1-phenyl-2-pyrazolin-5-one reagent saturated solution: Add 0.25 g of this compound to 50 mL distilled water, heat to 60°C with stirring. Cool to room temperature.

7.13.2.2 3,3'-dimethyl-1,1'-diphenyl-(4,4'-bi-2-pyrazoline)-5,5'-dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 mL pyridine.

7.13.2.3 Pour solution (7.13.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter pour solution (7.13.2.2), collecting the filtrate in the same container as the filtrate from (7.13.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but does not affect the color production with cyanide if used within 25 hours of preparation.

7.14 Magnesium chloride solution: Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1-liter flask, dissolve, and dilute to 1 liter with distilled water.

7.15 Boiling chips.

8. Procedure

8.1 Place 500 mL of sample, or an aliquot diluted to 500 mL in the 1-liter boiling flask. Add 50 mL of sodium hydroxide (7.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the vacuum train.

8.2 Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube. CAUTION: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.3 Slowly add 25 mL concentrated sulfuric acid (7.5) through the air inlet tube. Rinse the tube with distilled water and allow the air flow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride solution (7.14) into the air inlet tube and wash down with a stream of water. Add a few boiling chips through the air inlet tube and wash down with distilled water.

8.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one-half hour. Turn off the heat and continue the air flow for at least 15 minutes. After cooling the boiling flask, disconnect the absorber and close off the vacuum source.

8.5 Quantitatively transfer the solution from the absorber into a 100-mL volumetric flask.

8.6 This solution, or an aliquot of this solution, is then analyzed for cyanide using the titrimetric, colorimetric, or potentiometric methods of analysis.

8.7 Titrimetric method of analysis

8.7.1 If the sample contains more than 1 mg of CN^-, transfer the distillate, or a suitable aliquot diluted to 100mL to a 500-mL Erlenmeyer flask. Add 10-12 drops of the rhodanine indicator (7.11).

8.7.2 Titrate with standard silver nitrate (7.10) to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.7.3 The analyst should familiarize himself (herself) with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5- or 10-mL microburet may be conveniently used to obtain a more precise titration.

8.8 Colorimetric method of analysis

8.8.1 Withdraw 20 mL or less of the solution from the flask and transfer to a 100-mL volumetric flask. If less than 20mL is taken, dilute to 20 mL with 0.25 N sodium hydroxide solution (7.4). Add 6 mL of sodium phsophate solution (7.6) and mix.

8.8.1.1 Pyridine-barbituric acid method: Add 2mL of chloramine-T (7.12) and mix. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (7.13.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development, then read absorbance at 578 nm in a 1-cm cell within 15 minutes.

8.8.1.2 Pyridine-pyrazolone method: Add 0.5 mL chloramine-T (7.12) and mix. After 1 to 2 minutes, add 5 mL of pyridine-pyrazolone solution (7.13.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes read the absorbance at 620 nm in a 1-cm cell. NOTE: More than 0.5 mL chloramine-T will prevent the color from developing with pyridine-pyrazalone.

8.8.2 Prepare a series of standards by pipeting suitable volumes of standard solution into 100-mL volumetric flasks. To each standard add 50 mL of 1.25 N sodium hydroxide and dilute to 100 mI with distilled water. Prepare as follows:

mL of Standard Solution (5 μg/mL CN^-)	Concentration CN^- (mg CN^-/100 mL)
1	0.005
2.0	0.010
5.0	0.025
10.0	0.050
15.0	0.075
20.0	0.100

8.8.2.1 Prepare a standard curve by plotting absorbance of standard versus cyanide concentration.

8.8.2.2 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within ±10% of the undistilled standards, the operator should find the cause of the apparent error before proceeding.

8.8.3 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to ensure a level of 20 μg/L or a significant increase in absorbance value. Proceed with the analysis as in Section 8.1, using the same flask and system from which the previous sample was just distilled.

8.9 Potentiometric method of analysis

8.9.1 Prepare a series of standards by pipeting suitable volumes of a standard solution into 100-mL volumetric flasks. To each standard add 50 mL of 1.25 N NaOH and dilute to 100 mL with distilled water. Prepare as follows:

mL of Standard Solution	Concentration CN^- (mg CN^-/100mL)
(0.5 μg/mL CN^-)	
2.0	0.001
5.0	0.0025
10.0	0.005
(5 μg/mL CN^-)	
2.0	0.010
5.0	0.025
10.0	0.075
(50 μg/mL CN^-)	
2.0	0.100
5.0	0.25
10.0	0.50

8.9.1.1 Transfer the standard solutions into 150-mL beakers prerinsed with a small portion of the standard being tested. Immerse the cyanide and double junction reference electrodes in the solution and mix well on a magnetic stirrer. Maintain as closely as possible the same stirring rate and temperature for all solutions.

8.9.1.2 After equilibrium is reached (at least 5 minutes and not more than 10 minutes), record the millivolt reading and plot the CN^- concentrations versus millivolt reading on semilogarithmic paper. A straight line with a slope of 59 mV indicates that the instrument is operating properly.

8.9.1.3 It is not necessary that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If the distilled standards do not agree within ±10% of the undistilled standards, the operator should find the cause of the apparent error before proceeding.

8.9.2 Place the absorption liquid into a 150-mL beaker and proceed with the analysis as in Section 8.9.1. Determine the CN^- concentration by observing the millivolt reading and referring to the calibration curve established in Section 8.9.1. The method of known addition can be used for measuring occasional samples as the preparation of a caliabration curve is not required.

8.9.3 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to ensure a level of 20 µg/L or a significant increase in values. Proceed with the analysis as in Section 8.1, using the same flask and system from which the previous sample was just distilled.

9. Calculations

9.1 Using the titrimetric procedure, calculate the concentration of CN^- as follows:

$$CN^- \text{ (mg/L)} = \frac{(A-B)(1000)(100 \text{ mL})}{(\text{mL of original sample})(\text{mL of aliquot titrated})}$$

where:

A = Volume of $AgNO_3$ for titration of sample
B = Volume of $AgNO_3$ for titration of blank.

9.2 Using the colorimetric procedure, calculate the concentration of CN^- as follows:

$$CN^- \text{ (µg/L)} = \frac{(A)(1000)(100)}{(B)(C)}$$

where:

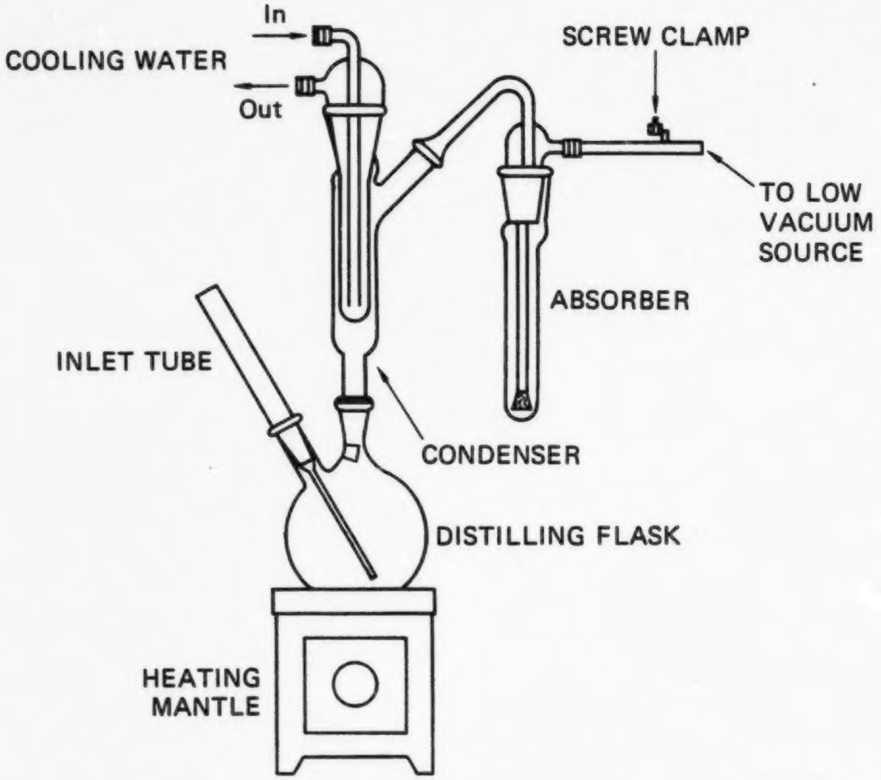
A = µg CN^- read from standard curve
B = mL of original sample taken for distillation
C = mL of scrubber solution taken for colorimetric analysis.

9.3 Using the potentiometric procedure, calculate the concentration of CN^- as follows:

$$CN^- \text{ (µg/L)} = \frac{(A)(1000)(100)}{(B)}$$

where:

A = µg CN^- read from standard curve
B = mL of original sample taken for distillation


In
COOLING WATER
Out
SCREW CLAMP
TO LOW VACUUM SOURCE
ABSORBER
INLET TUBE
CONDENSER
DISTILLING FLASK
HEATING MANTLE

SA-7854-23R

FIGURE 1 CYANIDE DISTILLATION APPARATUS

Appendix F

STATISTICAL PROTOCOL

1. Introduction

1.1 This appendix outlines the steps of the statistical protocol used in this study. The purpose of the statistical analysis is to estimate the total precision error of an analytical method.

2. Definitions and Symbols

2.1 Mean--arithmetic average $(\overline{X})$, defined as the sum of the observations divided by the number of observations (n).

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

2.2 Variance--σ^2, defined as the sum of the squares of the deviations from their mean (X) divided by one less than the number of observations (n - 1).

$$\sigma^2 = \frac{\sum_{i=1}^{n} \left(X_i - \overline{X}\right)^2}{n - 1}$$

2.3 Standard deviation--σ, defined as the positive square root of the variance (σ^2).

$$\sigma = \sqrt{\sigma^2}$$

2.4 Relative standard deviation (or coefficient of variation)--defined as the standard deviation divided by the mean.

$$\text{Relative standard deviation} = \frac{\sigma}{\overline{X}}$$

2.5 Grubb's test for rejection of an observation is applied to determine if one of the observations should be rejected as being an outlier. The following equation was used for the test:

$$B_1' = \left|\frac{X - \overline{X}}{\sigma}\right|$$

where:

X = observation being tested (most distant from mean)

$\overline{X}$ = mean of n observations

σ = standard deviation based on n - 1 degrees of freedom.

For any six observations, a value can be rejected if $B_1' \geq 1.944$. The B_1' limit is based on a 1% significance level (i.e., a B_1' calculated from the data can be expected to exceed 1.944 only 1% of the time if the observation is a legitimate one conforming to the underlying theory).

2.6 Lower limit of detection--defined as that level of cyanide in a sample, as KCN, where the percent relative standard deviation in a series of replicate analyses is found to be above 10% but below 50%.

$$0.1 \leq \text{relative standard deviation} \geq 0.5$$

In practice, the detection limit is governed not by the digestion/distillation step but by the finish used (i.e., ion-selective electrode, colorimetry or titrimetry). As such, the lower limit of detection reported here reflects the limitations of finishes used and their detection limits. It should be possible to extend the useful range of these procedures by suitable modification of the finish used here or by using a more sensitive finish.